PROGRAM RESULTS FROM A
COMPREHENSIVE ASSESSMENT OF
CHEMICAL EMISSIONS FROM
NEW YORK STATE ELECTRIC & GAS
CORPORATION'S MILLIKEN STATION
UNIT 2, LANSING, NEW YORK



From:

Daniel K. Hill <dhill@aesc.com>

To:

RTP3.RTMU546 (MAXWELL-BILL)

Date:

2/14/00 9:55am

Subject:

Re: AES Cayuga test information

MAXWELL.BILL@epamail.epa.gov writes:

>We have received both the original report (July 1997) and the

>supplemental, follow-up information

>(also dated July 1997), on the testing performed on the AES Cayuga

>(Milliken) facility. Your letter

>of May 28, 1999, indicates that we may consider the "report

>non-confidential for the purposes of

>the EPA." To avoid any confusion, I would appreciate a letter stating

>that this phrase applies to

>both reports/submittals. Thank you.

Bill-

As you have requested, please consider this email as authorization to to use both referenced reports as non-confidential. Dan

CC:

RTP6.RTPEML(GRIMLEY-WILLIAM), RTPMAINHUB.INTERNET("...

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PROGRAM RESULTS FROM A COMPREHENSIVE ASSESSMENT OF CHEMICAL EMISSIONS FROM NEW YORK STATE ELECTRIC & GAS CORPORATION'S MILLIKEN STATION UNIT 2, LANSING, NEW YORK

Prepared For:

NEW YORK STATE ELECTRIC & GAS CORPORATION Binghamton, New York

Prepared By:

Kusha D. Janati

CARNOTTustin, California

FINAL: JULY 1997



A

REVIEW AND CERTIFICATION

All work, calculations, and other activities and tasks performed and documented in this report were carried out under my direction and supervision.

____ Date _____6/6/97

Kusha D. Janati Senior Engineer

S. Cal. Emis. Measurement Div.

I have reviewed, technically and editorially, details, calculations, results, conclusions and other appropriate written material contained herein, and hereby certify that the presented material is authentic and accurate.

Kusha D. Janati Senior Engineer

S. Cal. Emis. Measurement Div.

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AAS Atomic Absorption Spectroscopy

APCD Air Pollution Control Device

ASTM American Society for Testing Materials

BIF Boiler and Industrial Furnaces

BrCl Bromine Monochloride

Btu British Thermal Unit

°C Degrees Celsius

CAAA Clean Air Act Amendments

CaCl₂ Calcium Chloride

CARB California Air Resources Board

CCTD Clean Coal Technology Demonstration

CE Combustion Engineering

CEMS Continuous Emissions Monitoring System

CI Confidence Interval

Cl⁻ Chloride

CO₂ Carbon Dioxide

CO Carbon Monoxide

CONSOL Inc. Research and Development

Cr⁶⁺ Hexavalent Chromium

Cr³⁺ Trivalent Chromium

CTE Commercial Testing and Engineering Company

CVAA Cold Vapor Atomic Absorption

CVAFS Cold Vapor Atomic Fluorescence Spectroscopy

DGA Double Gold Amalgamation

DI Deionized

DNPH 2,4-Dinitrophenylhydrazine

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DOE United States Department of Energy

DSCF Dry Standard Cubic Feet, 68°F and 1 atm

DSCFM Dry Standard Cubic Feet per Minute

ECTC Environmental Control Test Center

EDTA Ethylenediaminetetracetic Acid

EERC The Energy and Environmental Research Center

EPA See USEPA

EPRI Electric Power Research Institute

ESP Electrostatic Precipitator

°F Degrees Fahrenheit

F-Factor Fuel-Factor

FCEM Field Chemical Emissions Monitoring

FD Forced Draft

FeCl₃ Ferric Chloride

FGD Flue Gas Desulfurizer or Flue Gas Desulfurization

F Fluoride

g grams

GC Gas Chromatography

GFAAS Graphite Furnace Atomic Absorption Spectrometry

gpm gallons per minute

gr grains

H₂O₂ Hydrogen Peroxide

H₂SO₄ Sulfuric Acid

HCl Hydrochloric Acid

HDPE High-Density Polyethylene

HF Hydrofluoric Acid

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Hg(0)Elemental Mercury

Hg(II)Oxidized Mercury

HGAA Hydride Generation Atomic Absorption

HHV Higher Heating Value

HNO₃ Nitric Acid

HPLC High Performance Liquid Chromatography

HRGC High Resolution Gas Chromatography

HRMS High Resolution Mass Spectrometry

HxCDD Hexa-chlorinated Dibenzo-p-Dioxin

IC Ion Chromatography

ICP-AES Inductively Coupled Plasma-Atomic Emission Spectroscopy

ICP-MS Inductively Coupled Plasma-Mass Spectrometry

IC-PCR Ion Chromatography with Post Column Reaction

IN **ESP Inlet**

IR Infrared

ISE Ion-Selective Electrode

L or l liters

KC1 Potassium Chloride

kg Kilogram

klb 1000 pounds

KMnO₄ Potassium Permanganate

KOH Potassium Hydroxide

kW Kilowatt

lb Pound (mass)

LOI Loss On Ignition

LRMS Low-Resolution Mass Spectrometry

хi

 m^3

Cubic Meter

MCW

Maintenance Cleaning Water

MESA

Mercury Speciation Absorption

mg

milligrams

ml

milliliter

MM

Micron or Micrometer

MS

Mass Spectrometry

MW

Megawatt

MWe

Megawatt Net

MMBtu or 106Btu

Million Btu (see Btu)

N

Normal

 N_2

Nitrogen

NaHCO₃/Na₂CO₃

Sodium Carbonate/Sodium Bicarbonate

NBS

National Bureau of Standards

ND<

Non-detected less than

ng

nanograms

 Nm^3

Normal Cubic Meter, corrected to 0°C and 1 atm

NO,

Nitrogen Oxides

NYSEG

New York State Electric & Gas Corporation

10¹² Btu

Trillion Btu

ND

Not Detected

NDIR

Non-Dispersive Infrared

NH₃

Ammonia

NIST

National Institute of Standards and Testing

 O_2

Oxygen

OUT

ESP Outlet

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PAH

Polycyclic Aromatic Hydrocarbons

PCDD/PCDF

Polychlorinated Dibenzo-p-dioxins/Polychlorinated Dibenzofurans

PM

Particulate Matter

ppb

parts per billion

ppm

parts per million

PISCES

Power Plant Integrated Systems Chemical Emissions Studies

PSD

Particle Size Distribution

PVC

Polyvinyl Chloride

PWRF

Process Wastewater Reclamation Facility

QA

Quality Assurance

QC

Quality Control

RPDM

Relative Percent Difference from the Mean

RTI

Research Triangle Institute

S-H-U

Saarberg-Holter Umwelttechnik GmbH

Semi-VOST

Semi-Volatile Organic Sampling Train

SIM

Selective Ion-Monitoring

SO₂

Sulfur Dioxide

SO₃

Sulfuric Acid Mist

SO₄²-

Sulfate

SnCl₂

Stannous Chloride

STK

Stack

SW

Solid Waste

TCDD

Tetra-chlorinated Dibenzo-p-Dioxin

TDS/TSS

Total Dissolved Solids/Total Suspended Solids

TRIS

Tris (hydroxymethyl) aminomethane

USEPA

United States Environmental Protection Agency

DECLAS

xiii

UV

Ultraviolet

μg

micrograms

μm

micron or micrometer

VmStd

Sample Volume corrected to 68°F and 1 atm, dscf

VOC

Volatile Organic Compounds

VOST

Volatile Organic Sampling Train

WWTP

Wastewater Treatment Plant

Zenon

Zenon Environmental Laboratories

EXECUTIVE SUMMARY

As part of the Department of Energy's (DOE) Clean Coal Technology Demonstration (CCTD) Program, New York State Electric & Gas (NYSEG) Corporation has installed and is operating a high-efficiency flue gas desulfurization (FGD) system for SO₂ emissions control, low-NO_x burners for NO_x emissions control, and electrostatic precipitator (ESP) and coal mill upgrades for particulate emissions control. This installation was completed to demonstrate innovative emissions control technology. This demonstration program is being conducted at NYSEG's Milliken Station, Units 1 & 2, in the Town of Lansing, New York. The primary objective of this CCTD project is to show that a retrofit of energy-efficient SO₂, NO_x, and particulate control systems can be made without a significant impact on overall plant efficiency.

The FGD uses a forced oxidation, formic acid-enhanced wet limestone system to reduce SO_2 emission by 90-98%. Commercial-grade gypsum and calcium chloride salt are marketable by-products of the FGD's zero wastewater discharge process. Up to 40% NO_x reduction is achieved using the low- NO_x burners, and the ESP and coal mill upgrades reduced ESP outlet particulate levels by a factor of 10.

To satisfy DOE's CCTD program requirements, NYSEG, through a competitive bidding process, selected Carnot to conduct a comprehensive measurement program to characterize the emissions of selected trace substances from Milliken Station's Unit 2, both pre- and post-retrofit of SO_2 , NO_x , and particulate control systems. Prior to the pollution control system upgrades, Carnot performed a "baseline" comprehensive trace substance measurement program on Unit 2 in 1994. This report presents the results of the post-retrofit test program performed in August 1996 and compares them to baseline data.

To continue researching the viability and applicability of certain wet chemical techniques for collecting and subsequently detecting and quantifying species of mercury in coal-fired utility boiler flue gas streams, Carnot, under an extended contract with NYSEG with the cooperation and support of DOE, and the Energy & Environmental Research Center (EERC) at the University of North Dakota, under a separate contract with EPRI, performed a utility-scale field evaluation of two promising techniques, the Ontario-Hydro and TRIS Buffer, for mercury speciation. Since EPA Method 29 and Frontier Geosciences' solid sorbent scrubber technique were already part of the post-retrofit test program scope, by expanding the program to include the Ontario-Hydro and TRIS Buffer methods, EPRI, DOE and NYSEG were afforded the opportunity to compare all four mercury measurement techniques under full-scale conditions. Although EPA Method 29 and Frontier Geoscience have been used extensively to measure mercury on full-scale test programs, Ontario-Hydro and TRIS Buffer sampling methods have not been included. Prior

. 1

evaluations under bench- and pilot-scale conditions comparing these four methods have shown them to be in general agreement on total mercury.

EERC also operated a mercury instrumental analyzer at the FGD outlet/stack location. It should be noted that this test program did not attempt to evaluate all mercury speciation methods currently in development. This report also presents the results of these mercury speciation tests.

A summary of key post-retrofit test program results are provided in the following tables:

Table ES-1: Summary of Unit Operation and Criteria Pollutant Emissions Table ES-2: ESP and FGD Removal Efficiencies for Inorganic Species

Table ES-3: Summary of Detected Organic Species

Table ES-4: Summary of Mercury Speciation Test Results

Table ES-5: Comparison of Inorganic Element Flue Gas Emission Levels, Pre- and Post-Retrofit Test Programs

The following major conclusions were drawn from the results of this test program:

Flue Gas Test Results

- The ESP was effective at removing trace elements found primarily in the solidphase from the flue gas stream with an average removal efficiency of 99.7%. Major ash elements were effectively removed by the ESP at an average efficiency of 99.9%. The FGD removed trace elements at an average removal efficiency of 36.0%, and major elements at an average efficiency of 62.6%. The ESP removal efficiency for mercury was 16.7% and the FGD removal efficiency was 59.8%. Thus, overall removals by the ESP and scrubber combined were 99.81% for trace elements found primarily in the solid phase, 99.96% for major ash elements and 66.5% for mercury.
- With the exception of selenium, ESP inlet trace and major element results are in good agreement with coal input levels. From comparisons with coal input and flyash levels, selenium results for the ESP inlet and ESP outlet are severely biased low. Severe negative matrix interferences from the high levels of sulfur found in the ESP inlet and ESP outlet samples hindered their analyses for selenium. It is now believed that sulfur interferences are the main source for the low biases associated with the selenium analytical results for Milliken Unit 2. Given the low levels of sulfur contained in the stack EPA Method 29 samples and the lack of



matrix interferences encountered during analysis, the stack selenium results are considered valid.

- Reported hexavalent chromium results show that the ESP and FGD combined to remove hexavalent chromium from the flue gas stream at an efficiency of 26%. This efficiency is likely understated since the hexavalent chromium level at the stack was 4.2 times higher than the total chromium value measured by the EPA Method 29 sample train.
- The ESP removal efficiency for filterable particulate was 99.88%. ESP and coal mill upgrades for the post-retrofit test program reduced ESP outlet particulate concentrations by almost a factor of 10 when compared to pre-retrofit levels. Retrofit stack particulate emissions averaged 0.007 gr/dscf or 0.014 lb/106Btu.
- Chloride, fluoride and sulfur were found predominantly in the gaseous phase. The FGD was effective at removing chloride, fluoride and sulfur from the flue gas with average removal efficiencies of 99.4%, 98.7% and 93.1%, respectively. Mass balance results confirm particulate and anion flue gas concentration levels.
- For PAH emissions, only naphthalene, 2-methylnaphthalene, phenanthrene, and fluoranthene were measured at the stack at levels two times higher than the analytical detection limit or notably above field blank values. No dioxin or furan isomers were detected at levels greater than twice the field blank.
- Benzene concentrations measured at the ESP outlet averaged 2.3 ppb compared to 1.1 ppb at the stack. This difference across the FGD is not considered significant. Average toluene concentrations measured at the ESP outlet of 23 ppb were significantly higher than that of 7.2 ppb measured at the stack. It is not clear whether this difference is due to actual FGD removal or if it is just an artifact of measurement uncertainty.
- Stack formaldehyde emissions averaged 9.2 ppb which was 10 times higher than ESP outlet concentrations measured at 0.9 ppb. A possible source for the additional formaldehyde is the formic acid, which can have formaldehyde as an impurity, used by the FGD process. On the other hand, stack formaldehyde sample and field blank levels were similar.
- ESP outlet SO₃ concentrations were 5.8 ppm compared to 4.9 ppm at the stack.



• Particle size distribution at the ESP outlet averaged 76% less than 10 microns, 56% less than 2.5 microns, and 36% less than 1 micron.

Boiler/ESP and FGD Mass Balance Results

- In general, material balances were excellent for the post-retrofit test program. With the exception of selenium, all trace element and anion precursor (i.e. chlorine, fluorine, and sulfur) balances fell within the acceptable range of 70-130%, with most balances between 80-115%. All major element balances fell within the acceptable range of 80-120% range, with most between 90-110%.
- Excellent FGD balances can be seen for trace and major elements (including anion precursors) existing in the ESP outlet/FGD inlet flue gas at levels above 1 lb/10¹²Btu. For trace elements above this level in which an FGD balance could be reported, namely arsenic and mercury, balances ranged from 92-107%; for the major elements (excluding phosphorus and sodium), balances were consistently between 93-112%; and for the anion precursors, FGD closures fell within 97-102%.

Wastewater Treatment Plant Test Results

• WWTP removal efficiencies of around 75% or greater were seen for most target inorganic elements detected in the WWTP inlet stream. The treatment plant exhibited low removals for barium (12%), vanadium (46%), phosphorus (52%), and fluoride (46%). Negative or very low removals were seen for many of the water soluble elements (i.e. Ca, Mg, K, Na, Cl, S, N) suggesting that another input stream to the WWTP was a significant source of these elements, such as chemical treatment additives (e.g. lime and ferric chloride).

Mercury Speciation Test Results

• For the FGD outlet/stack location, excellent agreement between the Frontier Geoscience, Ontario-Hydro and TRIS Buffer measurements can be seen for Hg(0) and Hg(II). Hg(0) results ranged from 2.45-2.94 ug/Nm³ (excluding Method 29) and Hg(II) results ranged from 0.15-0.35 ug/Nm³ (excluding Method 29). Good to excellent agreement exists between Frontier, Ontario-Hydro, TRIS and EPA Method 29 for total mercury with results ranging from 2.66-3.29 ug/Nm³.



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- For the ESP outlet/FGD inlet, excellent agreement between Frontier, Ontario-Hydro, and TRIS can be seen for Hg(0) with levels ranging from 2.28-2.70 ug/Nm³.
- For the ESP outlet/FGD inlet, Ontario-Hydro and TRIS Buffer values are in good agreement for Hg(II); and Ontario-Hydro, TRIS and EPA Method 29 are in excellent agreement for total mercury.
- In comparison with the Ontario-Hydro and TRIS Buffer results, the EPA Method 29 mercury speciation values obtained from this test program exhibit a high bias for Hg(II), and a low bias for Hg(0).
- There is excellent agreement between the average FGD outlet/stack Hg(0) result as measured by the Semtech mercury analyzer with the other valid measurements at that location.
- FGD removal efficiencies were between 95-97% for Hg(II) (excluding EPA Method 29) and 59-65% for total mercury.
- Boiler/ESP mass balance results using Frontier Geoscience, Ontario-Hydro, TRIS Buffer, and EPA Method 29 total mercury values yielded 103%, 83%, 78%, and 85% agreement, respectively, between process streams.
- Total mercury FGD mass balance results for Frontier Geoscience, Ontario-Hydro, TRIS Buffer, and EPA Method 29 were 79%, 90%, 99%, and 93%, respectively.

Comparison Between Pre- and Post-Retrofit Test Programs

- The most notable difference between the baseline and post-retrofit test programs is that baseline testing was conducted while firing a 100% pre-cleaned coal, while a 50/50 mix between raw and pre-cleaned coal was burned during the post-retrofit program.
- The second most notable difference is that the upgrades to the ESP and coal mills improved particulate removal efficiency from 98.95% to 99.88%, reducing ESP outlet particulate concentrations by a factor of 10.
- A 45.4% NO_x reduction can be seen between the two test programs with baseline stack emissions falling from 452 ppm @ 3% O_2 to 247 ppm @ 3% O_2 .

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- Notable differences in fuel composition and unit operation between the test programs include an increase in fuel sulfur from 1.9% (baseline) to 2.3% (post-retrofit), an increase in fuel ash from 7.1% to 9.6%, and a higher boiler O₂ during baseline testing of 3.8% verses 3.1% for the post-retrofit program.
- For the ESP inlet, notable differences between concentration levels of target elements are consistent with those seen for the coal and flyash. It should be noted that ESP inlet and ESP outlet flue gas selenium levels for both test programs are severely biased low as a result of severe matrix interferences from sulfur. It should also be noted that pre-retrofit ESP outlet mercury level is biased high.
- Baseline ESP outlet particulate concentrations were reduced by 88% following the ESP and coal mill upgrades. This reduction in ESP outlet particulate levels directly corresponds to substantially reduced concentrations of trace and major elements exiting the ESP. Baseline ESP outlet trace element concentrations were reduced by 89% (excluding vapor phase elements of mercury, selenium, and anion precursors, in addition to molybdenum), and major element concentrations were reduced by 81%, for an overall reduction in trace and major elements of 86%.
- The large discrepancy between baseline and post-retrofit hexavalent chromium concentrations measured at the ESP inlet suggests that either one or both of the test programs' reported results are in error. Comparisons between mercury species flue gas results were not presented on Table ES-5 due to concerns regarding baseline mercury speciation data validity.
- The apparent increase in ESP outlet molybdenum concentrations for the postretrofit program is not representative of any actual changes in flue gas concentration; rather it is an artifact of blank corrections since molybdenum was found at blank levels for both programs.
- The FGD in combination with the upgraded ESP reduced trace and major element emissions slightly further with an overall reduction in baseline levels of 87% for the same group of elements (with the addition of magnesium). The FGD/ESP substantially reduced baseline mercury levels by 71% and baseline chloride, fluoride and sulfur levels by an average of 96%.
- Post-retrofit FGD outlet/stack emissions of magnesium were 53% higher than baseline emissions. This is most likely due to magnesium found within fugitive limestone particles exiting the FGD.



• For the volatile organic elements, the post-retrofit FGD and ESP upgrades combined to reduce baseline benzene emissions by 52%. However, post-retrofit FGD outlet/stack emissions of toluene and formaldehyde were 2-3 times higher than baseline emissions.

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TABLE ES-1 SUMMARY OF UNIT OPERATION AND CRITERIA POLLUTANT EMISSIONS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **AUGUST 1996**

Unit Type	CE, tangentially-fired
Fuel Type	Eastern Bituminous Coal
Fuel Sulfur Level	2.2-2.4%
Air Pollution	Low-NO _x Burners,
Control Devices	ESP & FGD

Test Period	Inorganic Elements	Organic Elements
	Measurement Period	Measurement Period
Test Dates	August 7-9, 1996	August 12-13, 1996
Unit Load, MWnet	149	140
Coal Flow Rate, klb/hr	118.7	148 120.7
Boiler O ₂ %	3.3%	
FGD Inlet Opacity, %	5.8	2.8% 6.0
SO ₂ , dry ppm @ 3% O ₂		
FGD Inlet	1805	1677
FGD Outlet	142	93
FGD Removal Efficiency	92.1%	94.4%
SO ₃ , dry ppm @ 3% O ₂		
FGD Inlet	6.8	NP
FGD Outlet	5.7	NP
FGD Removal Efficiency	15.3%	•••
NO _x , dry ppm @ 3% O ₂ (FGD Outlet)	. 227	267
NO _x , lb/10 ⁶ Btu (FGD Outlet)	0.304	0.357
Particulate Matter, lb/10 ⁶ Btu		
ESP Inlet	6.35	NP
ESP Outlet/FGD Inlet	0.007	NP
ESP Removal Efficiency	99.88%	- 14
FGD Outlet	0.014	NP

NP: measurement not performed during this test period

Note: Unit operating data and criteria pollutant emissions results are from Unit 2

operation logs except for SO₃ and Particulate Matter which are from Same temperature measurements operation logs except for SO₃ and Particulate Matter which are from Same temperature measurements.

TABLE ES-2
ESP AND FGD REMOVAL EFFICIENCIES FOR INORGANIC SPECIES
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Species		Inorganic Flue Gas Emissions, lb/1012Btu			FGD Removal	
	ESP INLET	ESP OUTLET	STACK	Efficiency	Efficiency	
Trace Elements						
Antimony	23	0.19	ND< 0.08	99.17%	> 57 79/	
Arsenic	489	1.7	0.91	99.65%	> 57.3%	
Barium	4.869	2.1	1.2	99.96%	47.3%	
Beryllium	52	0.03	0.02	99.94%	41.3%	
Cadmium	3.5	ND< 0.04	0.05	> 98.77%	31.4%	
Chromium	689	0.20	0.05	99.97%		
Hexavalent Chromium	0.85	NP	0.63	99.97%	25.0%	
Cobalt	183	0.12	0.63		25.9%	
Copper	475	0.90	0.12	99.94%		
Lead	309	0.56		99.81%	24.1%	
Manganese	1,373	0.61	0.63	99.82%		
Mercury	6.89		1.9	99.96%		
Molybdenum	97	5.74	2.31	16.75%	59.7%	
Nickel	528	0.39	0.35	99.60%	9.4%	
Selenium ⁽¹⁾		0.15	0.33	99.97%		
	26	35	21	NV	NV	
Vanadium	1,129	1.1	0.69	99.90%	39.1%	
nion Precursors						
Chlorine						
Solid Fraction	2,362	ND< 3.1	ND< 3.3	> 99.87%	••	
Gaseous Fraction	62,828	65,157	396		99.4%	
Total	65,190	65,159	398	0.05%	99.4%	
Fluorine			370	0.0370	27. 4 /0	
Solid Fraction	969	69.4	5.3	92.84%	92.3%	
Gaseous Fraction	5,592	6,423	80	72.0476	98.8%	
Total	6,561	6,492	85	1.05%		
Sulfur	,	5, . , 2	65	1.0370	98.7%	
Solid Fraction	28,372	1,126	2,082	96.03%		
Gaseous Fraction	1.84E+06	1.72E+06	1.17E+05	6.52%	03.30/	
Total	1.87E+06	1.73E+06	1.17E+05	7.88%	93.2% 93.1%	
_		11752.00	1.172.103	7.8876	93.1%	
articulate, lb/10 ⁶ Btu	6.35	0.007	0.014	99.88%		
lajor Elements	<u>lb/10⁶Btu</u>	<u>lb/10¹²Btu</u>	<u>lb/10¹²Btu</u>			
Aluminum	0.675	155	61	99.98%	60.6%	
Calcium	0.228	196	259	99.91%		
Iron	0.821	85	27	99.99%	68.6%	
Magnesium	0.037	15	104	99.96%		
Phosphorus	0.017	66	15	99.62%	76.5%	
Potassium	0.092	28	ND< 38	99.97%	76.5%	
Sodium '	0.038	108	141	99.72%		
Titanium			* . *	•	 44.7%	
	0.035	11	6.3	99.72% 99.97%		

ND<: parameter not detected

NP: measurement not performed

NV: not valid

Note: (1) From comparisons with coal feed and flyash levels, selenium results for the ESP inlet and outlet are severely biased low; subsequently ESP and FGD removal efficiencies are not valid for selenium.

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TABLE ES-3
SUMMARY OF DETECTED ORGANIC SPECIES
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

_	Trace Org	ganic Measurements,	lb/10 ¹² Btu	
Parameter	ESP Inlet	ESP Outlet	Stack	
Dolvovelie A nometic II-				
Polycyclic Aromatic Hy	· 			
Naphthalene	7.2	9.4	10	
2-Methylnaphthalene	Ò.028	0.027	0.23	
Acenaphthylene	ND< 0.002	0.003	ND< 0.006	
Acenaphthene	0.015	ND< 0.057	ND< 0.009	
Phenanthrene	0.003	ND< 0.022	0.10	
Anthracene	0.020	0.014	ND< 0.003	
PCDD/PCDF Isomers(1)	•			
2378-TCDD	ND< 1.5E-06	1.8E-06	1.7E-06	
12378 PeCDD	1.4E-06	1.2E-06	ND< 1.3E-06	
123478 HxCDD	3.7E-06	3.4E-06	3.2E-06	
1234678 HpCDD	2.1E-06	8.6E-07	ND< 2.1E-06	
OCDD	9.0E-06	3.4E-06	6.5E-06	
			0.52 00	
2378 TCDF	ND< 1.9E-06	ND< 7.5E-07	2.2E-06	
12378 PeCDF	8.5E-07	ND< 7.3E-07	ND< 5.8E-07	
23478 PeCDF	ND< 1.0E-06	ND< 8.6E-07	1.0E-06	
123789 HxCDF	2.9E-06	ND< 4.7E-06	3.1E-06	
OCDF	1.9E-06	ND< 1.1E-06	2.4E-06	
Volatile Organic Compo	unde			
Benzene	NP	6.7	• •	
Toluene .	NP		3.4	
Formaldehyde	NP	56	19	
	IAL	0.83	8.8	

ND<: species not detected

NP: measurement not performed

Note: (1) No PCDD or PCDF isomers were detected at levels greater than twice the field blank.

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TABLE ES-4 SUMMARY OF MERCURY SPECIATION TEST RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **AUGUST 1996**

Mercury Species	l'est Method	Emi	ssion Results, u	ESP Removal	ECD D	
		ESP Inlet	ESP Outlet/ FGD Inlet	FGD Outlet/ Stack	Efficiency ⁽¹⁾	Efficiency ⁽¹⁾
Hg(0) - Elemental	[
	EPA Method 29	0.80	1.49	2.40		
	Frontier Geoscience	2.12	2.66	2.40 2.94		
	Ontario-Hydro		2.28			
	TRIS Buffer		2.70	2.45		
	Semtech Hg 2000 Analyzer ⁽²⁾			2.71		
			NV	2.61		
Hg(II) - Oxidized						
	EPA Method 29	7.43	6.23	0.62	100/	
	Frontier Geoscience	6.93	6.82	0.35	18%	90%
	Ontario-Hydro		5.24		5%	95%
	TRIS Buffer		4.46	0.21		96%
			7.70	0.15		97%
Ig(total) - Hg Soli	<u>ds</u>					
	EPA Method 29	0.86	ND<0.009	0.006		
	Frontier Geoscience ⁽³⁾	0.06	0.07		99.5%	-
1	Ontario-Hydro		0.007	0.003	-	-
	TRIS Buffer		0.003	0.0009	_	
		_	0.002	0.004		-
OTAL Hg ⁽⁴⁾						
]	EPA Method 29	9.09	7.72	3.02	170/	
	Frontier Geoscience	9.11	9.56	3.02	17%	60%
(Ontario-Hydro		7.52	3.29 2.66		65%
7	TRIS Buffer		7.16			64%
	•		7.10	2.87	••	59%

NV -- results not valid. Semtech analyzer measurements performed at this location were deemed invalid due to the use of an improper sample conditioning system and detrimental ambient conditions (i.e. high temperature and dust level).

xxv

⁽¹⁾ Removal efficiencies calculated using emission units of lb/10¹²Btu to account for any differences in flue gas dilution

⁽²⁾ The Semtech Hg 2000 analyzer only measures elemental mercury.

⁽³⁾ The Frontier Geoscience method is not designed to representatively quantify the mercury solids fraction. These values represent mercury vapor that adsorbed on the flyash collected on the quartz wool plug during sampling. (4) Total Hg is the sum of Hg(0), Hg(II), and Hg solids.

TABLE ES-5 COMPARISON OF INORGANIC ELEMENT FLUE GAS EMISSION LEVELS PRE- AND POST-RETROFIT TEST PROGRAMS NYSEG MILLIKEN UNIT 2

Target		ESP INLET ⁽¹⁾			ESP OUTLET(2)			ET/STACK(3)
Parameter	Pre- Post-		Relative	Pre- Post-			Post-	EIISTACK
	Retrofit	Retrofit	Percent	Retrofit	Retrofit	Percent	Retrofit	Percent
	Conce	ntrations	Diff.	Conce	ntrations	Reduction ⁽⁴⁾	Concen.	Reduction ⁽⁵⁾
Particulate Matter, lb/10	⁶ Rtu							
	5.75	6.35	10%	0.060	0.007	88%	0.014	77%
Trace Elements, lb/1012B	<u>Stu</u>							
Antimony	30	23	26%	ND<0.51	0.19	_	ND<0.08	
Arsenic	475	489	3%	10	1.73	83%	0.91	
Barium	3,051	4,869	46%	8.4	2.1	75%	1.2	91%
Beryllium	72.3	52	32%	0.76	0.03	96%		85%
Cadmium	7.8	3.5	76%	0.34	ND<0.04	87%	0.02	97%
Chromium	894	689	26%	6.2	0.20	97%	0.05	84%
Hexavalent Chromium	8.6	0.85	164%	ND<0.07	NP	9/70	0.15	98%
Cobalt	198	183	8%	2.2	0.12	95%	0.63	
Copper	357	475	28%	4.2	0.12	79%	0.12	94%
Lead	276	309	11%	5.4	0.56	90%	0.69	84%
Manganese	928	1.373	39%	8.1	0.50	90%	0.63	88%
Mercury	6.4	6.89	7%	8.1	5.74	92% 29%	1.9	76%
Molybdenum	78	97	22%	0.17	0.39		2.31	71%
Nickel	592	528	11%	5.3	0.39	-129%	0.35	-108%
Selenium	58	26	76%	3.5		97%	0.33	94%
Vanadium	1,447	1,129	25%	12	35 1.1	-17% 91%	21 0.69	30% 94%
Anion Precursors, Ib/10 ¹²	Rtu							
Chlorine	64.476	65,190	1%	69,222	(6.150			
Fluorine	4.536	6.561	37%	4,259	65,159	6%	398	99%
Sulfur	,	1.87E+06	35%	-	6,492	-52%	85	98%
	1.512.00	1.072100	3376	1.36E+06	1.73E+06	-27%	1.19E+05	91%
Major Elements	16/10	⁶ Btu		lb/10	¹² Btu		lb/10 ¹² Btu	
Aluminum	0.624	0.675	8%	4,459	155	97%	61	99%
Calcium	0.097	0.228	80%	467	196	58%	259	45%
Iron	0.617	0.821	28%	2,634	85	97%	27	99%
Magnesium	0.024	0.037	45%	68	15	78%	104	-55%
Phosphorus	0.011	0.017	46%	155	66	58%	15	•33% 90% -
Potassium	0.069	0.092	29%	452	28	94%	ND<38	
Sodium	0.021	0.038	60%	364	108	70%	141	91%
Titanium	0.034	0.035	3%	208	11	70% 94%		61%
	_		J.•	200	11	7470	6.3	97%

Notes:

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⁽¹⁾ ESP INLET = flue gas concentrations at the boiler exit or inlet to the ESP.

⁽²⁾ ESP OUTLET = flue gas concentrations at the outlet of the ESP; for the pre-retrofit test program the ESP Outlet and Stack are syn sample locations.

⁽³⁾ FGD OUTLET/STACK = FGD outlet flue gas emissions; only applicable to the post-retrofit test program.

⁽⁴⁾ Percent Reduction of flue gas emissions due to the ESP upgrades = (Pre-Retrofit ESP Outlet Level - Post-Retrofit ESP Outlet Level)/Pre-Retrofit ESP Outlet Level

⁽⁵⁾ Percent Reduction of flue gas emissions due to the combined effect of the ESP upgrades and FGD = (Pre-Retrofit ESP Outlet Level - Post-Retrofit Stack Level)/Pre-Retrofit ESP Outlet Level

SECTION 1.0

INTRODUCTION

1.1 TEST PROGRAM BACKGROUND

The Clean Air Act Amendments (CAAA) of 1990 require the Environmental Protection Agency (EPA) to conduct an assessment of health and environmental effects posed by the emissions of 189 trace chemicals from electric utility steam generating units. Although mercury is only one of the targeted trace chemicals potentially emitted to the atmosphere by utilities, EPA has singled it out for a separate emissions and risk assessment study.

As part of the Department of Energy's (DOE) Clean Coal Technology Demonstration (CCTD) Program, New York State Electric & Gas (NYSEG) Corporation has installed and is operating a high-efficiency flue gas desulfurization (FGD) system for SO₂ emissions control, low-NO_x burners for NO_x emissions control, and electrostatic precipitator (ESP) and coal mill upgrades for particulate emissions control. The installation was completed to demonstrate innovative emissions control technology. This demonstration program is being conducted at NYSEG's Milliken Station, Units 1 & 2, in the Town of Lansing, New York. The primary objective of this CCTD project is to show that a retrofit of energy-efficient SO₂, NO_x, and particulate control systems can be made without a significant impact on overall plant efficiency.

The FGD uses a forced oxidation, formic acid-enhanced wet limestone system to reduce SO_2 emission by 90-98%. Commercial-grade gypsum and calcium chloride salt are marketable by-products of the FGD's zero wastewater discharge process. Up to 40% NO_x reduction is achieved using the low- NO_x burners, and the ESP and coal mill upgrades reduced ESP outlet particulate levels by a factor of 10.

To satisfy DOE's CCTD program requirements, NYSEG, through a competitive bidding process, selected Carnot to conduct a comprehensive measurement program to characterize the emissions of selected trace substances from Milliken Station's Unit 2, both pre- and post-retrofit of SO₂, NO_x, and particulate control systems. Prior to the pollution control system upgrades, Carnot performed a "baseline" comprehensive trace substance measurement program on Unit 2 in 1994. This report presents the results of the post-retrofit test program performed in August 1996 and compares them to baseline data.

Since 1990, the Electric Power Research Institute (EPRI) and DOE have initiated programs to develop chemical emissions databases for the utility industry. More recently both



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groups have focussed their efforts on developing a measurement technique for the various species of mercury in utility combustion flue gas streams. Based on a formal validation study sponsored by EPRI, it was determined that EPA Method 29 can produce reliable measurement data for total mercury concentrations in coal combustion flue gas. A major methods development program of certain promising techniques for the collection and subsequent detection and quantification of various mercury species is currently being conducted by EPRI and DOE, in cooperation with EPA. This effort has involved intensive bench-scale and pilot-scale testing, in addition to limited utility-scale evaluations.

To continue researching the viability and applicability of these measurement techniques for measuring mercury species in coal-fired utility boiler flue gas streams, Carnot, under an extended contract with NYSEG with the cooperation and support of DOE, and the Energy & Environmental Research Center (EERC) at the University of North Dakota, under a separate contract with EPRI, performed a utility-scale field evaluation of two emerging techniques, the Ontario-Hydro and TRIS Buffer, for mercury speciation. Since EPA Method 29 and Frontier Geosciences' solid sorbent scrubber technique were already part of the post-retrofit test program scope, by expanding the program to include the Ontario-Hydro and TRIS Buffer methods, EPRI, DOE and NYSEG were afforded the opportunity to compare all four mercury measurement techniques under full-scale conditions. Although EPA Method 29 and Frontier Geoscience have been used extensively to measure mercury on full-scale test programs, Ontario-Hydro and TRIS Buffer sampling methods have not been included. Prior evaluations under bench- and pilot-scale conditions comparing these four methods have shown them to be in general agreement on total mercury.

EPA Method 29, Frontier Geoscience, Ontario-Hydro, and TRIS Buffer have undergone and are currently undergoing intensive bench- and pilot-scale evaluations by EERC at their University of North Dakota test center under the sponsorship of EPRI and DOE. While concerns exist whether EPA Method 29 and Frontier Geoscience can accurately quantify mercury species, the EERC results to date indicate that the Ontario-Hydro and TRIS Buffer methods are promising techniques to accurately measure Hg(II) and Hg(0), in addition to total mercury, in simulated coal-fired flue gas streams. The protocols for these methods developed by EERC were followed by Carnot at the Milliken Station.

EERC also operated a mercury instrume al analyzer at the FGD outlet/stack location. It should be noted that this test program did real attempt to evaluate all mercury speciation methods currently in development. This reposition also presents the results of these mercury speciation tests.



1.2 TEST PROGRAM OBJECTIVES

The following objectives of the NYSEG Milliken Unit 2 Post-Retrofit Chemical Emissions Characterization Program were accomplished:

- Characterize stack emissions of selected inorganic elements, target anions, and volatile and semi-volatile organics at normal full load operating conditions with the retrofit SO₂, NO_x, and particulate control systems in operation.
- Simultaneously measure criteria and non-criteria pollutant levels entering and exiting the power plant's ESP and FGD to evaluate their effectiveness at removing various chemical substances.
- Calculate boiler, ESP, and FGD material balances for target inorganic elements by examining their distribution levels across various input/output process streams.
- Perform mercury and chromium speciation tests at the flue gas sampling locations to provide additional data on these trace substances.
- Compare the post-retrofit chemical emission data set to that generated from the baseline field sampling study performed on Unit 2 in May 1994.
 - Evaluate the wastewater treatment plant's performance at removing target inorganic elements from the coal pile run-off by examining their levels in the plant's inlet and outlet effluent.
 - Provide data on chemical substance levels in the power plant's solid stream output and wastewater discharge streams, namely, ash, gypsum solids, FGD blowdown heavy metal sludge, metals treatment plant sludge, calcium chloride brine product and the Process Wastewater Reclamation Facility (PWRF) outlet.
 - Perform a utility-scale field evaluation of the Ontario-Hydro and TRIS Buffer mercury speciation sampling methods.

- Evaluate the performance of a Semtech Hg 2000 analyzer (owned by EPRI), a realtime continuous emissions mercury analyzer, at the FGD outlet/stack sampling location.
- Compare daily and average Hg(0), Hg(II), and total Hg results from the Ontario-Hydro, TRIS Buffer, Semtech Hg 2000 analyzer, Frontier Geosciences' solid sorbent scrubber, and EPA Method 29 mercury measurement techniques.
- Provide ESP and FGD removal efficiencies for targeted mercury species from each of the measurement techniques employed.

1.3 PROCESS DESCRIPTION

The NYSEG Milliken Station is composed of two identical, tangentially-fired, Combustion Engineering boilers with a nominal generating capacity of 150 MW each and associated pollution abatement equipment. Unit 2 was evaluated in this program while it burned a 2.2-2.4% sulfur, Pittsburg seam, bituminous coal. Low NO_x burners, an ESP, and an FGD provide Unit 2 with NO_x, particulate, and SO₂ emissions control, respectively. A detailed unit description can be found in Section 2.1.

1.4 TARGET POLLUTANTS

Table 1 lists the generic classes of substances that were measured on each process stream sampled during the Milliken Unit 2 chemical emissions test program. Table 2 presents the particular pollutants included in each class. These substances were targeted based on input from NYSEG, DOE and EPRI. The compounds include most of the 189 compounds listed as hazardous air pollutants (HAPs) under Title III of the 1990 CAAA.

1.5 SAMPLING APPROACH

Representative samples from the following process streams were collected and analyzed according to Tables 1-1 and 1-2:

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TABLE 1-1
TEST MATRIX BY PROCESS STREAM
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

Fire Gas Sample Streams Solid Sample Streams Outlet ESP Stream Solid Sample Streams Outlet ESP Stream Outlet Outle						Boiler/L	SP/FGD	Boiler/ESP/FGD Process Streams	ams				Wastew	Wastewater Treatment Plant Process Streams	nt Plant Prov	ore Streame
ESP Bieck Coal Pointer Feed Ash Ash Selida Solida Coal Product Shelps Runoff Read Ash Ash Selida Solida Coal Product Shelps Runoff Runoff Read Ash Runoff Ru		Flue G	as Samp	le Streams		Sol	d Sample	Streams		Liquid/Slu	dge Sam	ple Streams				200
	Target Compounds	ESP			Coal	8888	ESP Fly	Limeatons	•	FVARE	Brine	Heavy Mils	Coal Pile	Heavy Mitts	Heavy Mitis	Heave Mile
		¥ E			Feed		Ash	Settids	Solids	Outtet 1	roduct	Sludge	Runoff	Trut inlet	Trmt Outle	Trent Sludge
	1. Trace Elements	×	×	×	×	×	×	¥	×	•	>			,	;	
e	2. Hexavalent Chromium	×		×							<		<	•	<	Ž
	3. Mercury Speciation Tests										80(80)					
X	2a. Frontier Geoscience	*	×	*							****					
Deficit X	2b. Ontario-Hydro		×	×	-						848 8					
Varietic X	2c. TRIS Buffer		×	×												
Compounds	2d. Semtech IIg 2000 Analyzer			×							388					
Compounds X	3. Solid Particulate/Ash Content		×	×	×	×	×	*	×		\$ \$					
Compounds X	4. Major Elements		×	×	×	×	×	×	×	×	×	×	×		×	4
X	5. Acid-forming Anion Precursors		×	×	×	×	×	×	×		×	¥	×		× >	
tion X X X X X X X X X X X X X X X X X X X	6. Semi-Volatile Organic Compounds														•	•
tion X X X X X X X X X X X X X X X X X X X	6a. PAH		×	*												
	6b. PCDD/PCDF		×	*												
tion X X X X X X X X X X X X X X X X X X X	7. Volatile Organic Compounds															
tion X X X I I I I I I I I I I I I I I I I	7a. Benzene and Toluene		×													
tion X X X Interest X X X X X X X X X X X X X X X X X X X	7b. Formaldehyde		×	×												
tion X	8. Sulfuric Acid Mist		×	×												
int CEMS) X X X X X X X X X X X X X X X X X X X	9. Particle Sizing Distribution		×								388					
	10. CEMS Data															
nalysis X X X X X X X X X X X X X X X X X X	10a. NO., SO2, CO2 (Plant CEMS)		×	×												
nalysis X X X X X X X X X X X X X X X X X X	10b. Diluent Gases - O1*	×	×	×												
X	11. Ultimate/Proximate Analysis				×	×	×	*	×		**************************************					
	12. Higher Heating Value				×											
*	13. Moisture	*	× 		×	×	×	×	×		### 					

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TABLE 1-2 TARGET COMPOUND LIST NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

	TRACE ELEMENTS	
Antimony	Arsenic	Barium
Beryllium	Cadmium	Chromium (by two methods) ²
Cobalt	Copper	Lead
Manganese	Mercury (by five methods) ¹	Molybdenum
Nickel	Phosphorus	Selenium
Vanadium -		
	MAJOR ELEMENTS	
Aluminum	Calcium	Iron
Magnesium	Potassium	Silicon
Sodium		Titanium
AC.	D-FORMING ANIONS OR PREC	CURSORS
Chloride	Fluoride	Sulfur
SE	MI-VOLATILE ORGANIC COM	POUNDS
	Polýcyclic Aromatic Hydrocarb	ons :
Acenaphthene	Acenaphthylene	Anthracene
Benz(a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene
Benzo(g,h,i)perylene	Benzo(k)fluoranthene	Chrysene
Dibenzo(a,h)anthracene	Fluoranthene	Fluorene
Indeno(1,2,3-cd)pyrene	Naphthalene	Phenanthrene
Pyrene	2-Methylnaphthalene	3-Methylcholanthrene
	7,12-Dimenthylbenz(a)anthracene	-
Polychlorinate	d Dibenzo-p-dioxins and Polychlor	inated Dibenzofurans
	l for tetra-through octa-chlorinated h	
	All 2,3,7,8 substituted isomers	3
	VOLATILE ORGANIC COMPO	UNDS
Benzene	Toluene	Formaldehyde
	MISCELLANEOUS COMPOU	NDS
Total Particulate	Particle Sizing	Sulfur Oxides
from the Frontier Geosciences, measuring Hg(0).	EPA Method 29 multi-metals sample train, and Hg(0) Ontario-Hydro, and TRIS Buffer sampling trains. A poly I from the EPA Method 29 train and hexavalent chromi	rtable mercury analyzer was used at the stack for

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Boiler/ESP/FGD Process Streams (triplicate samples)

Flue Gas Sample Streams

- 1. ESP Inlet
- 2. ESP Outlet (FGD Inlet)
- 3. Stack (FGD Outlet)

Solid Sample Streams

- 1. Coal Feed
- 2. Bottom Ash
- 3. ESP Flyash
- 4. Limestone Solids
- 5. Gypsum Solids

FGD Liquid/Sludge Sample Streams

- 1. PWRF Outlet (to FGD absorber module)
- 2. Brine Product
- 3. FGD Heavy Metal Sludge (duplicate samples)

Wastewater Treatment Plant Process Streams (duplicate samples)

- 1. Coal Pile Run-off
- 2. Heavy Metals Treatment Plant Inlet
- 3. Heavy Metals Treatment Plant Outlet
- 4. Heavy Metals Treatment Plant Sludge

1.6 PROGRAM ORGANIZATION

Carnot was the prime contractor for the NYSEG chemical emission field test program. EERC, under a separate contract with EPRI, prepared, recovered, and performed the mercury speciation analyses of the Ontario-Hydro and TRIS sampling trains, in addition to operating the Semtech Hg 2000 instrumental analyzer. Zenon Environmental Laboratories was a major subcontractor to Carnot that provided a majority of the program's analytical services. Mr. Mehdi Rahimi and Mr. Walt Savichky are NYSEG's program managers for this study. EPRI serves as a technical consultant. The project team organization is identified in Figure 1-1.

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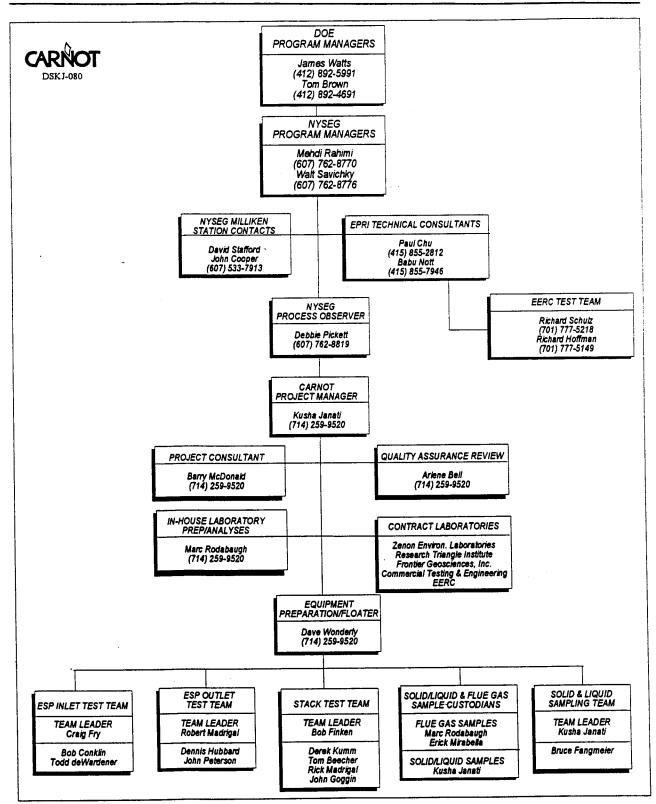


Figure 1-1. Project Team Organization Chart

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1.7 DATA USE AND DATA CONFIDENTIALITY

The data generated from this test program are intended for use by NYSEG, DOE and EPRI for assessment and planning purposes. All sampling and analyses were conducted according to Carnot's approved July 1996 final test plan (Report Number NYS1A-11476/R107G264.T), which was developed using Carnot's May 1994 Milliken Unit 2 baseline report, EPRI's established FCEM PISCES protocol, and EERC's mercury speciation method protocols. Results generated by this field study are targeted to meet "compliance" quality standards.

The information generated on this program is treated by Carnot and its subcontract laboratories, and EERC as confidential. It will only be released to other parties at the expressed wishes of NYSEG.

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SECTION 2.0

TEST DESCRIPTION

This section presents a description of Milliken Station's Unit 2 and the different sample locations that were used for the test program, followed by a review of the test schedule and process operation during testing.

2.1 UNIT DESCRIPTION

The Milliken Station is located in the Town of Lansing, New York and is owned and operated by the NYSEG Corporation. Milliken Station Unit 1 and 2 were built in the late 1950s. The units are Combustion Engineering designed, tangentially-fired, pulverized coal boilers. Unit 2 has a design capacity of 1,145,000 lbs/hr steam at 1900 psig and 1005°F with a nominal generating capacity of 150 MW. Up to 40% NO_x reduction is achieved using CE LNCFS-III low-NO_x burners which were installed in 1994. The Unit 2 boiler is equipped with an ABB Heat Pipe air heater and a wide-spaced, rigid frame ESP manufactured by Belco, which was also installed in 1994. In addition, a Saarberg-Holter Umwelttechnik GmbH (S-H-U) flue gas desulfurization (FGD) process was installed and began operating at Milliken Station Unit 2 in January, 1995. The process is a forced oxidation, formic acid-enhanced wet limestone scrubber designed to reduce SO₂ emissions by 90% to 98%. The exhaust gas is discharged to the atmosphere through a wet flue without reheat. The plant has high dispatch priority and is generally base loaded. The capacity factor is typically >80%. This unit is among the most efficient in the United States.

The coal is delivered to Unit 2 from a common coal pile that serves both boilers. During this test program, Unit 2 burned a Pittsburg seam, bituminous coal containing 2.2% - 2.4% sulfur that was a 50/50 mix of raw and cleaned coal. The coal mills were upgraded in 1994 and produce no rejects.

Bottom ash is sluiced out to the bottom ash solids sedimentation basin where the solids are dewatered and removed from the plant site by truck. The bottom ash sluice water is recirculated in a closed loop. Make-up water from the lake intake is periodically added to maintain the liquid level of the sedimentation tank. The ESP flyash is pneumatically conveyed to a storage silo, then removed from the plant site by truck for use as a portland cement pozzolonic additive.



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Commercial-grade gypsum and calcium chloride salt are marketable by-products of the FGD's zero wastewater discharge process. During this test program, however, the brine concentrator was not in operation so the unconcentrated brine product was discharged to the PWRF for disposal to the lake. Gypsum is transported by conveyor belt to a gypsum storage building for subsequent loading onto trucks. Heavy metals are removed from the scrubber water blowdown, producing a sludge that is trucked for disposal.

The Milliken Station process wastewater generated from Units 1 and 2 is treated at the PWRF before returning to the lake. The coal pile runoff is collected in a first-stage catch basin located near the coal pile. The collected coal pile runoff is treated in the metals treatment plant located adjacent to the PWRF. The out-fall of the metals treatment plant discharges to the PWRF before returning to the lake. Sludge generated by the PWRF and metals treatment plant are removed from the station by truck for on-site disposal.

2.2 SAMPLE LOCATIONS AND COLLECTION PROCEDURES

Figure 2-1 is a process flow diagram for Unit 2 depicting the boiler/ESP/FGD system. Figure 2-2 provides a more detailed process flow description of the FGD system. Solid dots represent sampling locations for the flue gas, solids, and liquid/sludge sample streams.

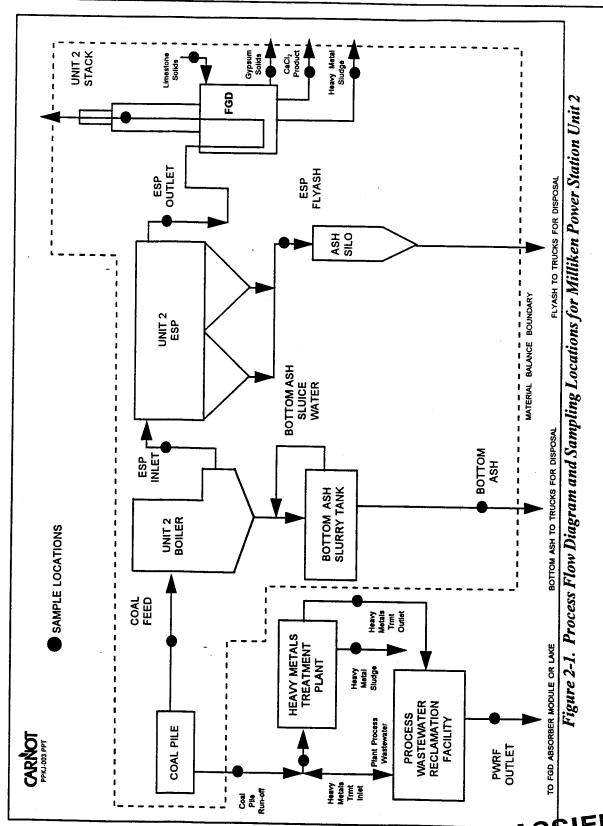
2.2.1 Flue Gas Sample Streams

The primary sample streams of interest for the Milliken Unit 2 test program were the flue gas streams entering and exiting the ESP and FGD air pollution control devices (APCDs). An objective of this research study was to determine the effectiveness of these APCDs at removing targeted pollutants released during coal combustion.

Tests requiring a full traverse of the sampling location collected flue gas at each of the prescribed sampling points. The number and location of sampling points that were used at the ESP inlet and outlet were based on the ESP inlet sampling grid used for the May 1994 baseline test program given the current location of existing port obstructions. The stack sampling grid was based on EPA Method 1 criteria. Tests conducted within a single port at the ESP inlet and outlet (either 1-3 sample points) alternated between the North and South ducts (except VOST). Stack single- point tests were performed at the same representative sampling point for each replicate.



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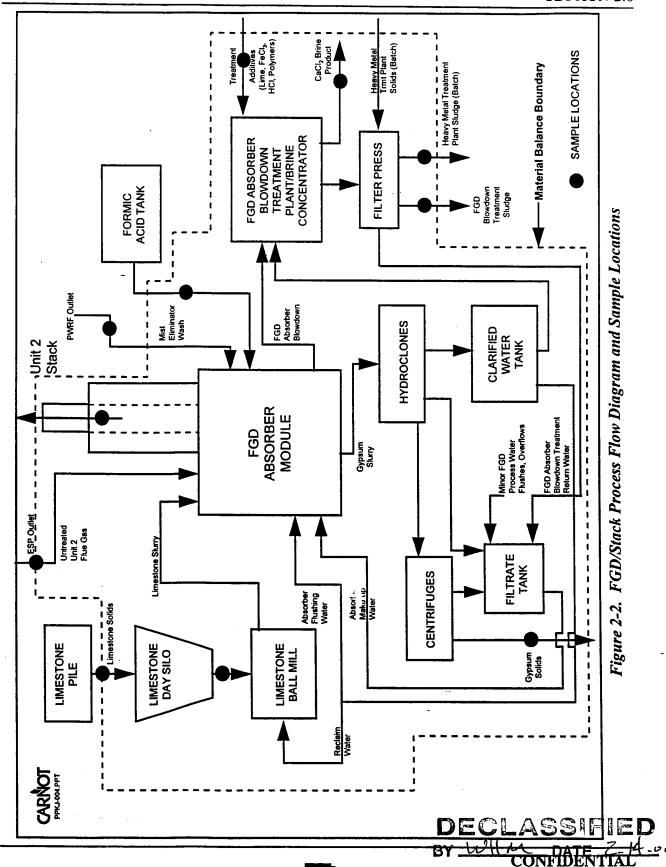


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2.2.1.1 **Unit 2 ESP Inlet**

The ESP inlet location consists of two vertical ducts, each one 3 feet 6 inches deep by 33 feet 9 inches wide. The sample ports are located 80 feet (12.7 diameters) downstream and 40 feet (6.3 diameters) upstream of the nearest flow disturbances, satisfying EPA Method 1 minimum requirements for an acceptable sample location. Figure 2-3 presents a side-view of the ESP inlet sample location. There are 24 ports total, 12 per duct, designated as Ports A through X as shown in Figure 2-4. Seven of the ports, E, K, N, O, T, V, and X, were not available for sampling due to port obstructions.

Prior to testing, a full velocity traverse was performed through all 24 sample ports. EPA Method 1 requires a minimum of 12 traverse points per duct or 24 points total. The decision to use three sample points per port was judged technically sound during Carnot's May 1994 baseline test program based on the duct depth, and is consistent with previous ESP performance testing conducted by CONSOL. The preliminary velocity data were analyzed to select 8 sample ports (to provide a total of 24 points) that produce an average flue gas velocity that is representative of the overall duct velocity, but spaced-out enough to cover the entire duct length adequately. Figure 2-4 identifies which ports were chosen for the full-traverse isokinetic tests. This 8-port grid resulted in an average velocity that was 2.5% different from the entire 24-port velocity. The sample grid used at the ESP inlet is similar to the one used for the May 1994 baseline tests. Exhaust gas flow rates from the pitot traverses of the post-retrofit tests using this sampling grid agreed well (2-4% average differences) with those calculated from boiler efficiency, unit load, and an EPA Method 19 stoichiometric F-factor.

No cyclonic flow was measured at this location using EPA Method 1 indicating that a laminar flue gas flow profile exists.

2.2.1.2 Unit 2 ESP Outlet

The Unit 2 ESP outlet location (inlet of the FGD) is a mirror image of the ESP inlet location with identical measurements and sampling scheme. Figure 2-5 illustrates the sampling grid for the ESP outlet. Nine of the ports, A, C, E, I, M, N, Q, T, and X, were not available for sampling due to port obstructions.

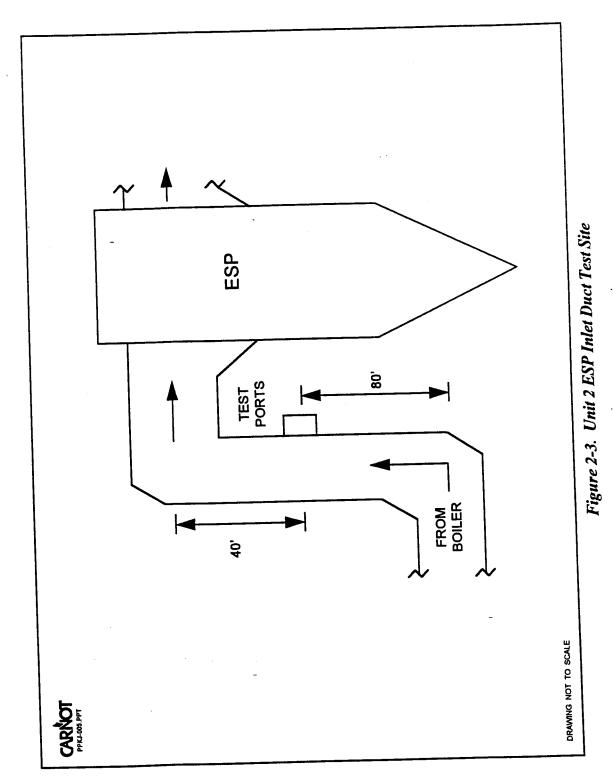
A full velocity traverse was performed prior to testing through 23 of the 24 ports (one port cap was frozen shut). As identified on Figure 2-5, 8-ports were chosen for a 24-point total sample grid similar to the ESP inlet. This 8-port grid resulted in an average velocity that was 4.7% different from the overall 23-port velocity. Due to the numerous obstructions present at this location, no other port scheme for sampling could be found that provided a more representative velocity and still maintain satisfactory spacing across the ducts. Exhaust gas flow

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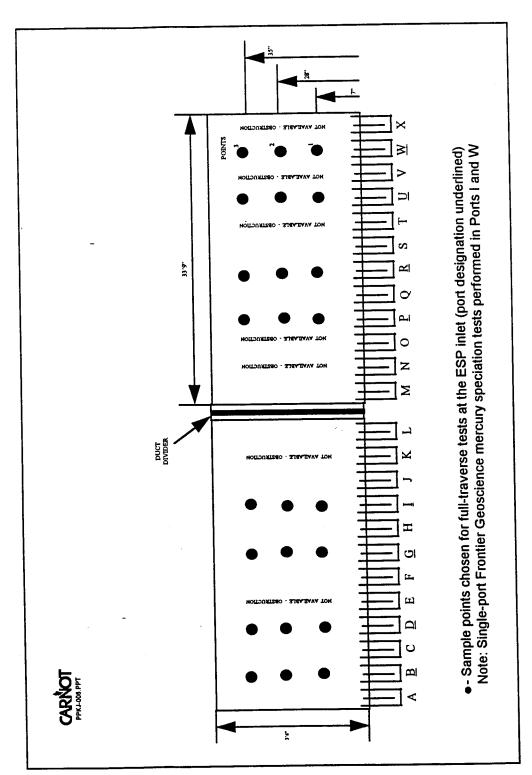
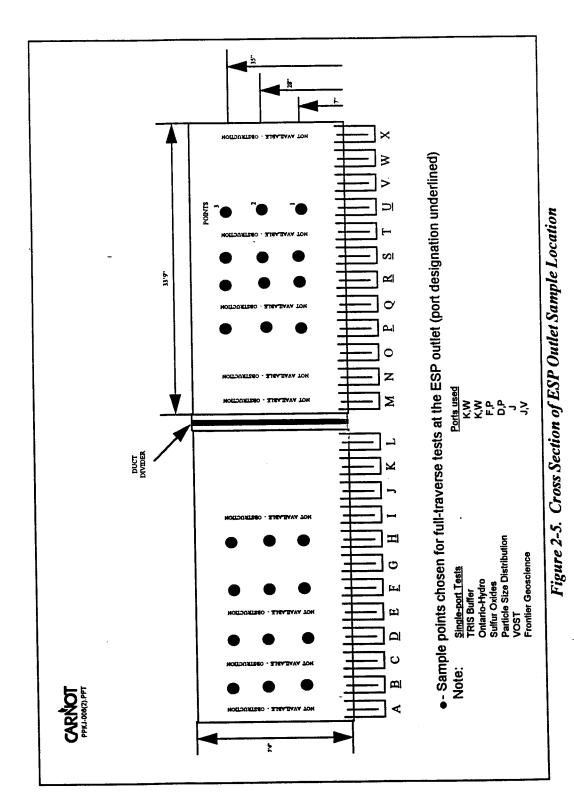


Figure 2-4. Cross Section of ESP Inlet Sample Location

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rates from the pitot traverses of the ESP outlet tests using this sample grid agreed well (0-4% average differences) with EPA Method 19 calculated flow rates.

Less than one degree of cyclonic flow was measured at this location (20° maximum cyclonic flow is allowed by EPA Method 1), indicating that a laminar flow profile exists.

2.2.1.3 Stack

Figure 2-6 provides a profile of the Unit 2 flue test site and presents traverse point locations. The Unit 2 flue (FGD outlet stream) discharge point is approximately 375' from ground level and the stack sampling plane is located 304' from ground level. Figure 2-7 illustrates a cross-sectional view of the FGD stack location showing all three flues within the larger stack. Two identical 12 foot diameter flues each serving Unit 1 and 2, along with a smaller 8 foot diameter emergency bypass flue, are located inside the 40 foot diameter stack. Two sampling ports located at 90° offsets with coupling lengths of 6" were used for full traverse tests. A third sampling port offset 90° from one of the main sampling ports was used for single-point tests.

This location meets EPA Method 1 minimum requirements with almost 6 diameters upstream and 13 diameters downstream of the nearest flow disturbances; as a result, 12 sample points, 6 per port were used. Less than two degrees of cyclonic flow was found at this location indicating laminar flow.

2.2.2 Solid Sample Streams

To substantiate the flue gas data, coal feed, bottom ash, ESP flyash, limestone solids, and gypsum solids samples were collected throughout the test program. The samples were analyzed for target inorganic elements and balanced with flue gas data in an attempt to obtain mass balance closure. Table 2-1 provides a solid stream sampling schedule.

2.2.2.1 **Coal Feed**

Pulverized coal combined with combustion air is injected into the boiler through a series of burners supplied by four coal mills. Coal is supplied to each mill by belt feeders drawing coal from the bunkers. Only three mills are necessary for full-load operation. During this test program one coal mill was not in service. As-fired coal samples representative of a complete cross-section of the unpulverized coal feed to the mills was obtained using each belt feeder's coal sampling system. After activating the coal sampling system, a 5 lb sample is provided within one minute.

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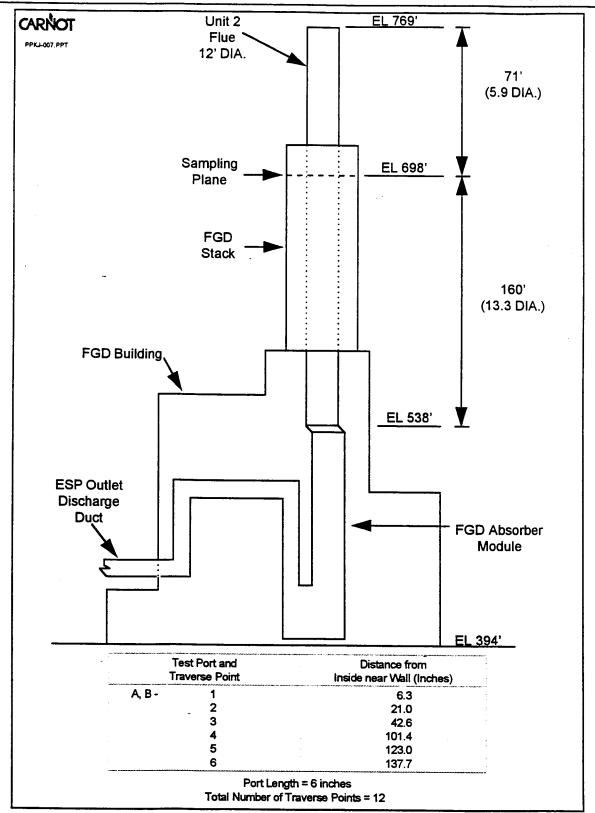


Figure 2-6. Stack Test Site and Traverse Point Location DECLASSIFIED

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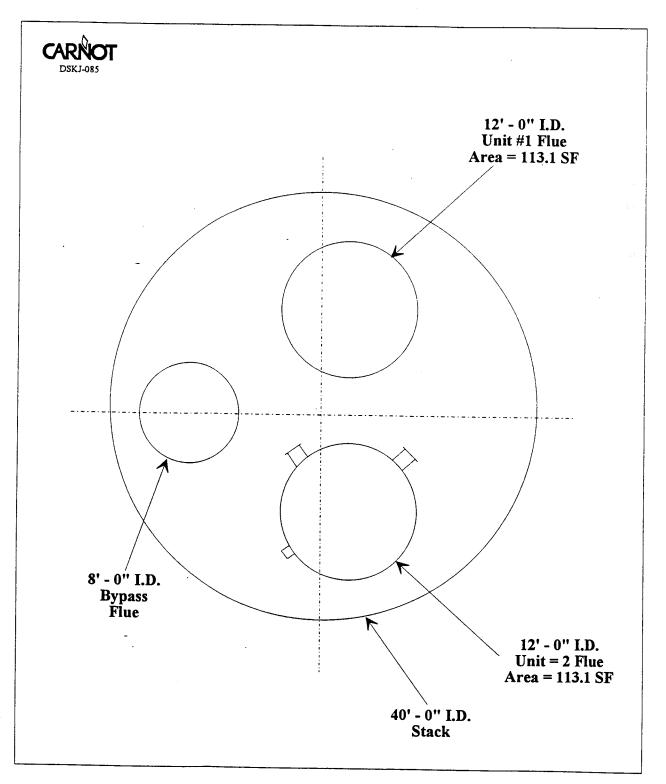


Figure 2-7. Cross-Sectional Area - Units 1 & 2 FGD Stack

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TABLE 2-1 SOLID AND LIQUID/SLUDGE STREAM SAMPLING SCHEDULE NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM AUGUST 1996

Test	Date	Sample	Type of	Sample Top	No. of	Increment	Gross Sample	Number	Sample Size	Sample	No. of
Number		Time	Sample	Size, in. (1)	Increments	Size. Ibs.	Weight, lbs.	of Splits	to Lab. lbs. (2)	Container	Containers
								·			
1-COAL	8/7/96	815/1545	Raw/Clean Coal	<5/8	24	5	120	2	30	HDPE Bck.	1
2-COAL	8/8/96	805/1545	Raw/Clean Coal	∹5/8	24	5	120	2	30	HDPE Bck.	1
3-COAL	8/9/96	805/1545	Raw/Clean Coal	<5/8	24	5	120	2	30	HDPE Bck.	1
4,5-COAL	8/12/96	910/1900	Raw/Clean Coal	<5/8	18	5	90	1/3,2/3	30 each	HDPE Bck.	2
6-COAL	8/13/96	910/1530	Raw/Clean Coal	< 5/8	12	5	60	1	30	HDPE Bck.	1
1-BottomAsh	8/7/96	1800	Bottom Ash	<-2	14	6.9	96	0	96	HDPE Bck.	2
2-BottomAsh	8/8/96	1830	Bottom Ash	<:2	14	5.9	82	0	82	HDPE Bck.	2
3-BottomAsh	8/9/96	1645	Bottom Ash	<2	14	6.5	91	0	91	HDPE Bck.	2
1-Flyash	8/7/96	910/1610	ESP Flyash	-60 mesh	7	1-17 (3)	47	6	50 grams each	120 ml	6
2-Flyash	8/8/96	909/1620	ESP Flyash	-60 mesh	8	0.5-30	101.5	7	50 grams each	glass jars	6
3-Flyash	8/9/96	919/1500	ESP Flyash	-60 mesh	6	5-46	133	7	50 grams each	w/ plast. lids	6
I-Limestone	8/7/96	1830	Limest'n Solids	<:2	25	4.3	107	0	107	HDPE Bck.	2
2-Limestone	8/8/96	1330	Limest'n Solids	:: <u>2</u>	25	4.7	118	0	118	HDPE Bck.	2
3-Limestone	8/9/96	1430	Limest'n Solids	<2	24	4.3	104	0	104	HDPE Bck.	2
l-Gypsum	8/7/96	821/1429	Gypsum Solids	-8 mesh	7	10-11	74	3	9 .	Plastic Bag	1
2-Gypsum	8/8/96	930/1330	Gypsum Solids	-8 mesh	3	24-25	73	3	10	Plastic Bag	1
3-Gypsum	8/9/9 6	1005/1445	Gypsum Solids	-8 mesh	3	24-25	74	3	10	Plastic Bag	1
I-FGD Sludge	8/8/96	750/825	FGD Sludge	NA	8	1	8	0	8	Plastic Bag	2
2-FGD Sludge	8/9/96	810/830	FGD Sludge	NA	8	0.38	3	0	3	Plastic Bag	2
1-Brine	8/7/96	1446/1620	Brine Product	NA	3	400 ml	1.2 liters	0	500 ml. x 2	AW-500ml	2
2-Brine	8/8/96	808/1613	Brine Product	NA	9	400 ml	3.6 liters	0	500 ml. x 2	AW-500ml	2
3-Brine	8/9/96	800/1517	Brine Product	NA	8	400 ml	3.2 liters	0	500 ml. x 2	AW-500ml	2
I-PWRF	8/7/96	801/1610	PWRF Outlet	NA	9	400 ml	3.6 liters	0	500 ml. x 2	AW-500ml	2
2-PWRF	8/8/9 6	805/1610	PWRF Outlet	NA	9	400 ml	3.6 liters	0	500 ml. x 2	AW-500ml	2
3-PWRF	8/9/96	756/1513	PWRF Outlet	NA	8	400 mi	3.2 liters	0	500 ml. x 2	AW-500ml	2
I-WWTP IN	9/9/96	1600/2400	WWTP Inlet	NA	9	400 ml	3.6 liters	0	500 ml. x 2	AW-500ml	2
2-WWTP IN	9/9/96	1600/2400	WWTP Inlet	NA	9	400 ml	3.6 liters	0	500 ml. x 2	AW-500ml	2
-wwtp out	9/9/96	1600/2400	WWTP Outlet	NA	9	400 mi	3.6 liters	0	500 ml. x 2	AW-500ml	2
2-WWTP OUT	9/9/96	1600/2400	WWTP Outlet	NA	9	400 mi	3.6 liters	0	500 ml. x 2	AW-500ml	2
-Coalpile	9/9/96	1600/2400	Coalpile Run-Off	NA	9	400 ml	3.6 liters	.0	500 ml. x 2	AW-500ml	2
2-Coalpile	9/9/96	1600/2400	Coalpile Run-Off	NA	9	400 ml	3.6 liters	0	500 ml <u>.</u> x 2	AW-500ml	2
l-Sludge	9/10/96	1000	WWTP Sludge	NA	8	200 grams	3.5	0	3.5	Plastic Bag	2
2-Sludge	9/10/96	1030	WWTP Sludge	NA	8	200 grams	3.5	0	3.5	Plastic Bag	2

NA - not applicable

HDPE - high density polyethylene

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AW -- acid-washed HDPE Nalgene sample bottles

All solid stream sample collection and preparation procedures were in accordance with ASTM D2234 and ASTM D2013.

⁽¹⁾ Sample top size defined as smallest screen opening in which less than 5% of sample is retained.

⁽²⁾ Minimum sample size for laboratory analysis based on ASTM D2234.

⁽³⁾ Isokinetic sampling of the flyash resulted in varying increment sample sizes based on ESP hopper evacuation intervals. Each increment was riffled on-site to a sample size less than or equal to 50 grams and composited with other 50 gram increments from that test period to obtain a single 50 gram test sample.

The coal burned during this test program was a 50/50 split of raw and pre-cleaned bituminous coal, pre-crushed to a top size of less than 5/8 inch and supplied by CONSOL from its Pittsburgh seam. ASTM D2234 specifications for the collection of pre-cleaned coal was used during the post-retrofit test program, which call for a minimum of 15 sampling increments of at least two pounds each for a total minimum sample size of 30 pounds to be taken. For the inorganic test period (8/7-9/96), each belt feeder sampler was activated once per hour over a seven to eight-hour period providing 24 increments and a gross sample size of approximately 120 pounds. For gross sample sizes of more than 30 pounds ASTM D2234 allows for the sample to be properly size reduced to 30 pounds, e.g. riffled, before any reduction in the sample top size is necessary. Two sample splits were made on-site using the plant's large rifflers in accordance with ASTM D2013. Using the pre-cleaned coal collection procedure, as opposed to the one for raw coal (which would require 35 increments) or an average of the two (25 increments), was considered appropriate based on the 5 pound increment sample size and the resulting gross sample size of 120 pounds. Coal samples obtained during the organic test period (8/12-13/96) were for ultimate/proximate analysis only and, as such, were not collected as frequently for a total of 12-18 increments.

COAL FLOW MEASUREMENTS. As the coal travels from the coal bunkers to the mills, a gravimetric scale on each mill belt feeder determines the weight of coal that passes over the belt scale section. A digital totalizer on each mill tracks the amount of coal supplied to the mills. NYSEG quality assurance testing of the new belt feeders revealed that they are not capable of providing reliable fuel flow data "as-delivered." The vendor is currently working to correct this flow measurement problem and is scheduled to complete the re-work by June 1997. As a result, an alternate method of calculating the fuel flow rates was performed. Pitot flow rates from the ESP outlet EPA Method 29 and semi-VOST tests were determined to accurately represent flue gas flow rates at this location, and were combined with a calculated EPA Method 19 F-factor to obtain fuel flow rates.

2.2.2.2 **Bottom Ash**

Bottom ash from Unit 2 is batch sluiced approximately once per shift and conveyed to a hydrobin where the bottom ash solids are dewatered. The sluice procedure takes about 30 minutes. The liquids used in sluicing are continually recirculated in a closed-loop system that is assumed to be at equilibrium with the bottom ash solids and therefore an insignificant output stream of target trace elements. Solids are periodically emptied from the bottom ash storage silo into a transport truck and dumped at an off-site disposal area for use as an anti-skid material. Obtaining a "dry" bottom ash sample prior to the sluicing operation is not possible; therefore, representative samples were collected from the pile after the bottom ash solids are dumped.

Prior to the start of each day's test activities for the inorganic test period, the bottom ash was sluiced and the solids in the hydrobin emptied. Throughout the test day, the ash was sluiced normally. Following testing, the sluiced bottom ash solids were emptied into the transport truck, dumped at the off-site disposal area, and sampled that day. The bottom ash pile was divided into 14 cross-sections and one 6-7 pound increment shovel full was removed from the center of each cross-section. The entire daily gross sample was sent to the laboratory in two plastic buckets.

BOTTOM ASH FLOW MEASUREMENTS. The total weight of bottom ash generated for each test day was determined by obtaining a tare and final weight of the transport truck. NYSEG and the transport company conducted the weighings.

2.2.2.3 - ESP Flyash

The ESP is equipped with eight hoppers. The collected flyash from each hopper is periodically emptied and conveyed to a storage silo. An insitu sampler designed by CONSOL to collect a representative ash sample automatically extracts flyash isokinetically from the main discharge line between the ESP hoppers and storage silo. Prior to the start of each test day, the hoppers were emptied. Throughout the test day, the hoppers were evacuated into the silo in accordance with normal operation.

As hoppers discharge during each inorganic test day, representative flyash sample increments were collected into clean 5-gallon plastic buckets by the extractive sampling system. Following a 45-60 minute sampling interval, the bucket located inside the extractive system was replaced with an empty one. Increment sample sizes varied from 0.5 to 46 pounds depending on hopper discharge cycles. Six to 8 increments were collected over a 6-7 hour test period.

Each increment was size reduced as necessary and combined with the other daily increments. The flyash top size is assumed to be at most -60 mesh so daily samples were riffled according to ASTM D2013 to six 50 gram portions stored in 120 ml glass jars for each test day.

ESP FLYASH FLOW MEASUREMENTS. ESP flyash flow rates were calculated from the EPA Method 5 particulate test results from the ESP inlet and outlet.

2.2.2.4 Limestone Solids

From the limestone pile located outside of the FGD building, conveyor belts transport limestone to day silos that can store up to a 2-day supply of material. Limestone from the day silos are conveyed through belt feeders and dropped into ball mills where it is crushed and combined with reclaim water (gypsum slurry water) to obtain limestone slurry. Storage tanks provide a constant stream of limestone slurry to the absorber modules. Since the same limestone

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slurry is sent to both Unit 1 and Unit 2's absorbers, no attempt was made to isolate the limestone solids intended for Unit 2 from those intended for Unit 1.

Samples of the limestone solids were collected from an intermediate pile located near the main limestone pile outside the FGD building. The intermediate pile was formed each day by tractor above a hopper supplying limestone to the day silo conveyor belts. The perimeter of the pile was divided into 24-25 cross-sections and 4-5 pound shovel full increments were removed from the center of each cross-section. The entire daily gross sample was sent to the laboratory in two plastic buckets.

The limestone is considered to be fairly uniform and homogeneous. As a result, the collection of limestone prior to the day silo as opposed to prior to the absorber is not expected to affect the representative nature of the limestone samples.

LIMESTONE SOLID FLOW RATE. Hourly limestone slurry flow rates into the Unit 2 absorber module and percent slurry solids values were averaged over each daily test period from FGD control room data logs. The limestone solids flow rate into the absorber was then calculated by combining the average slurry flow rate and density results.

2.2.2.5 Gypsum Solids

The gypsum slurry leaving the Unit 2 absorber is first treated by the primary hydroclones to separate out the larger particles (gypsum solids) which are dewatered in the centrifuges to produce the gypsum product. After primary hydroclone separation, the overflow slurry is treated by secondary hydroclones which produce clarified water (clear) consisting of only very fine particles. The clarified water may either return to the limestone ball mills as reclaim water, the absorber module as flushing water, or the FGD blowdown treatment plant. The secondary hydroclone underflow stream consists of medium size particles (untreated limestone) and small gypsum crystals which are combined with the filtrate that was removed by the centrifuges and stored in the filtrate tank which is sent directly to the absorber module.

Unit 2 gypsum product is removed from the FGD building by a conveyor to an enclosed building for off-site truck removal. Unit 2 centrifuges produce gypsum in batches every 15 minutes and were isolated from Unit 1's gypsum solids. The gypsum solids contained 8-9% moisture. A plastic scoop was used to collect a complete cross-section of the gypsum solids as they fell from the baskets onto the conveying system. For the first day of the inorganic test period, seven 10-11 pound increments were collected. For the second and third days, only three increments were collected at 24-25 pounds each due to intermittent gypsum solids production. Daily gross sample sizes of 73-74 pounds were coned, quartered and split using a large plastic tarp. Nine to 10 pound daily samples were sent to the laboratory in plastic bags.

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GYPSUM SOLIDS FLOW RATE. The gypsum solids flow rate was calculated as the difference between the average flow rate of gypsum slurry entering the centrifuges and that leaving, combined with an average slurry percent solids value. There is no feasible method for determining the amount of solids that are separated with the gypsum water by the centrifuges and sent to the filtrate tank. As a result this means of calculating a gypsum solids flow rate slightly over-estimates gypsum output. Based on a solids mass balance around the FGD process, however, this over-estimation was considered negligible. Centrifuge flow rates and gypsum slurry density values were averaged over each daily test period from FGD control room data logs.

2.2.3 FGD Liquid/Sludge Sample Streams

FGD input and output liquid/sludge process streams were sampled in an effort to close the FGD mass balance for targeted inorganic elements. These process streams are common to the desulfurization of both Unit 1 and Unit 2's flue gas. There was no way to isolate Unit 2 from Unit 1 for these process streams, as a result, flow rates were adjusted proportionally based on net MW output from both units.

As part of FGD blowdown and clarified water treatment, certain chemical additives are introduced such as lime (neutralization), ferric chloride (coagulation), and polymers (flocculation). In addition, HCl is added for brine concentration. The polymer additive is not considered a significant input stream for target elements and HCl was not added since the brine concentrator was out of service. Lime and ferric chloride additives are considered significant input streams for calcium, iron and chlorine. To account for them, typical flow rates for these additive streams obtained from plant personnel were combined with product specifications for CaO and FeCl₃ concentration levels, along with stream density values, to calculate input flow rates for these elements.

2.2.3.1 PWRF Outlet Water

Process Wastewater Reclamation Facility (PWRF) outlet samples were obtained from a pre-existing tap on the lake discharge line. A 400-ml increment sample was collected into a high-density polyethylene (HDPE) sample bottle approximately every hour during the inorganic test period over the course of an eight-hour test window (0800 to 1600 hours). Increments were combined into a HDPE 1-gallon container and 2-500 ml composites were removed for trace elements and anion analyses. The composite for trace elements was treated with nitric acid to obtain a pH level of 2 and both the metals and anion composites were stored at 4°C in accordance with standard sample preservation requirements of EPA SW846 methodologies. Flow rates for this stream were taken from plant instrumentation.



2.2.3.2 Brine Product

FGD blowdown and clarified water from the gypsum slurry secondary hydroclones are sent through a continuous treatment process that removes solids and metal hydroxides to produce a brine product stream. A brine concentrator is being demonstrated as a removal technique for chlorides that produces a marketable CaCl₂ salt. The distillate water from the brine concentrator can then be recycled back to the FGD absorber make-up water tank. During this test program, however, the brine concentrator was not in operation. Samples of the brine product stream were collected prior to its discharge into the plant's PWRF system. Samples were collected in the same manner as the PWRF outlet water samples during the inorganic test period. Flow rates for this stream were taken from FGD control room data logs.

2.2.3.3 FGD Blowdown Treatment Heavy Metal Sludge

The solids and metal hydroxides contained in the FGD blowdown and clarified water streams removed by the treatment process are sent to a filter press that produces a heavy metal sludge. The sludge is deposited into a large bin and trucked off-site for landfill disposal. A single filter press operation produces one load of sludge in 4 hours. For this test program, sludge production was set-up to be a continuous operation that produced approximately 6 loads per day. FGD sludge production was suspended after the second day due to operational problems. Sludge samples were extracted from the sludge pile on the mornings of 8/8/96 and 8/9/96 corresponding to sludge produced the day before. Using a 1" PVC pipe approximately 10 foot long, four to sixinch long core samples were obtained at 4 sample points spaced along the center axis of the pile. Two core samples were taken at each sample point (for a total of eight core samples), first with the PVC pipe oriented vertically and second with the pipe at an angle of approximately 60°. Increment weights ranged from 0.4 to 1 pound based on sludge moisture levels. Increments were combined for a total daily sample size of 3-8 pounds and stored at <4°C, as per EPA SW846 protocols, before shipping to the laboratory. The sludge bin was emptied before the test program began and then weighed after the second day of sludge production. The flow rate for forty-eight hours of sludge was proportionally corrected to isolate Unit 2 production from Unit 1 based on unit load distribution.

2.2.4 <u>Wastewater Treatment Plant Sample Streams</u>

The heavy metal wastewater treatment plant inlet and outlet streams were sampled to determine the plant's heavy metal treatment removal efficiency. The coal-pile runoff was sampled to determine its contribution to the heavy metals treatment plant inlet stream. Wastewater treatment sludge samples were taken to determine their general composition as a disposal stream. WWTP samples were taken by plant personnel on 9/9/96 and 9/10/96 following

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the completion of the main test program after heavy rains produced enough coal-pile run-off to bring the treatment plant on-line.

2.2.4.1 **Coal-Pile Runoff**

Coal-pile runoff drains into the first-stage catch basin (coal-pile runoff pond) before being sent to the maintenance cleaning water (MCW) holding pond. Samples of the coal-pile runoff were dipped out of the first-stage catch basin in the same manner as the PWRF outlet samples. Coal-pile runoff is sent to the MCW basin in batches, as needed, and therefore flow rates for this process stream are meaningless.

2.2.4.2 Heavy Metal Treatment Plant Inlet/Outlet

Inlet samples from the MCW holding pond were collected from a tap located on the metals treatment plant inlet line in the same manner as the PWRF outlet water samples.

Outlet samples to the PWRF were collected from the treatment plant outlet weir box in the same manner as the PWRF outlet water samples.

Flow rates for both process streams were obtained from plant data logs.

2.2.4.3 Wastewater Treatment Sludge

The wastewater treatment sludge is produced by the same filter press as the FGD sludge. Following treatment of the coal-pile runoff on 9/9/96, the treatment sludge was batch produced on 9/10/96 and sampled in the same manner as the FGD sludge. No flow rate for this stream was obtained.

2.3 TEST SCHEDULE

Table 2-2 presents the flue gas sampling schedule for the inorganic test period. One test replicate was performed for each method per day at each appropriate sample location simultaneously over the course of three days. Test 1-MESA-IN performed on 8/7/96 was lost after the test was completed, so two Frontier Geoscience replicates (test numbers 3 & 3A) were performed on 8/9/96 at each location in order to have a complete set of simultaneous data. Test 2-SO3-STK was voided due to sampling problems and repeated that same day. Four sulfur oxide replicates were performed at the stack in case one set of results were found to be suspect. The particulate/anion test time of 120 minutes for the first ESP inlet run was increased to 240 minutes for the remaining two runs to simplify sampling logistics.

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TABLE 2-2
FLUE GAS SAMPLING SCHEDULE -- INORGANIC TEST PERIOD
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

			Sample Times	
Test No.	Date, 1996	ESP Inlet	ESP Outlet/FGD Inlet	FGD Outlet/Stack
Trace and Major Element	nts:			
I-MTLS	7-Aug	0817/1227	0833/1512	0817/1441
2-MTLS	8-Aug	0803/1212	0822/1435	0811/1540
3-MTLS	9-Aug	0803/1210	0814/1435	0815/1507
Particulate/Anions:				0015/1507
I-PM/AN	7-Aug	1044/1249	0927/1357	0818/1230
2-PM/AN	8-Aug	0844/1255	0854/1258	0802/1215
3-PM/AN	9-Aug	0915/1320	0821/1254	0802/1213
Frontier Geoscience Me			0021/1254	0814/1230
1-MESA	7-Aug	Sample Voided	1025/1325	1050/1250
2-MESA	, 8-Aug	0840/1040	0845/1145	1050/1350
3-MESA	9-Aug	0930/1140	0845/1145	0845/1145
3A-MESA	9-Aug	1340/1540	1245/1545	0827/1127
Ontario-Hydro Mercury		1340/1540	1243/1343	1215/1515
I-OH-OUT	7-Aug		0840/1440	
2-OH-OUT	8-Aug		0756/1356	0842/1442
3-OH-OUT	9-Aug		0817/1417	0753/1353
Tris Buffer Mercury Spe			001//141/	0826/1426
1-TRIS	7-Aug		1533/1633	16164
2-TRIS	8-Aug		· · - •	1515/1715
3-TRIS	9-Aug		1417/1517	1425/1625
Sulfur Oxides:	/ rug		1432/1532	1520/1720
1-SO3	7-Aug		1542/1742	
2-SO3-OUT	8-Aug		1543/1643	1545/1730
2B-SO3-STK	8-Aug		1336/1436	Sample Voided
3A-SO3	9-Aug		1225/1425	1610/1730
3B-SO3-STK	9-Aug		1335/1435	1300/1420
Particle Size Distribution	·			1505/1615
1-PSD-OUT	7-Aug		1/1///	
2-PSD-OUT	8-Aug		1615/1715	
3-PSD-OUT	9-Aug		1415/1545	
	7-Aug		1315/1445_	

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TABLE 2-3

FLUE GAS SAMPLING SCHEDULE -- ORGANIC TEST PERIOD

NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

AUGUST 1996

			Sample Times	
Test No.	Date, 1996	ESP Inlet	ESP Outlet/FGD Inlet	FGD Outlet/Stack
Semi-Volatile Organics:				
1-SV -	08/12/96	0851/1255	0851/1256	0918/1327
2-SV	08/12/96	1540/1944	1443/1852	1510/1920
3-SV	08/13/96	0820/1225	0832/1240	0835/1245
Hexavalent Chromium:				
1-CR	08/12/96	1246/1454		1240/1540
2-CR	08/13/96	0954/1244		0830/1130
3-CR	08/13/96	1449/1701		1445/1745
Formaldehyde:				
1-FORM	08/13/96		1200/1402	1215/1420
2-FORM	08/13/96		1401/1606	1345/1550
3-FORM	08/13/96		1601/1816	1605/1810
VOST:				
IA-VOST	08/12/96		1450/1510	1450/1510
1B-VOST	08/12/96		1525/1545	1525/1545
1C-VOST	08/12/96		1559/1619	1559/1619
1D-VOST	08/12/96		1630/1650	1630/1650
2A-VOST	08/12/96		1709/1729	1709/1729
2B-VOST	08/12/96		1739/1759	1739/1759
2C-VOST	08/12/96		1808/1828	1808/1828
2D-VOST	08/12/96		1842/1902	1842/1902
3A-VOST	08/13/96		1144/1204	1144/1204
3B-VOST	08/13/96		1212/1232	1212/1232
3C-VOST	08/13/96		1242/1302	1242/1302
3D-VOST-OUT	08/13/96		1322/1342	
3E-VOST-STK	08/13/96			1357/1417

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Table 2-3 presents the flue gas sampling schedule for the organic test period. Most test replicates were performed over the course of two days, 8/12/96 and 8/13/96, except those for formaldehyde which were completed all in a single day on 8/13/96.

A separate test schedule showing only the mercury speciation tests is given on Table 2-4. All mercury speciation tests were performed on August 7, 8, and 9, 1996. EPA Method 29 and the Ontario-Hydro sampling trains were operated at the ESP outlet/FGD inlet and FGD outlet/stack locations simultaneously for 360 minutes. The TRIS Buffer sample trains were operated following the completion of the Ontario-Hydro testing. TRIS Buffer sampling was conducted for 60 minutes at the ESP outlet/FGD inlet and for 120 minutes at the FGD outlet/stack. The Semtech Hg 2000 analyzer was operated each day of the mercury measurements over time intervals that corresponded to Ontario-Hydro and TRIS Buffer sampling periods.

Table 2-1 gave the sampling schedule for the solid and liquid/sludge process streams. Most sampling was performed during the inorganic test period between 8/7/96 and 8/9/96 for mass balance purposes. Coal samples were also collected during the organic test period on 8/12/96 and 8/13/96. Wastewater Treatment Plant sampling occurred on 9/9/96 and 9/10/96 following heavy rains which produced enough coal-pile run-off to bring the treatment plant online.

2.4 PROCESS OPERATION DURING TESTING

Table 2-5 summarizes the process operating conditions for the inorganic and organic test periods. Operation of Unit 2 during this test program was representative of normal daily operation at or near full load. Opacity levels were in compliance and no ESP operating problems were identified. To obtain maximum uniformity and the most representative samples, steady-state process conditions were maintained throughout each test day with variations in unit load, excess oxygen, and ESP power levels well within acceptable tolerances. Prior to each test day, key operating parameters were stabilized, the bottom ash storage silo was emptied, and the ESP hoppers evacuated.

Unit Load. Load on Unit 2 during this test program was steady within an average range of 147-150 net MW. Main steam flows were around 1100 Klb/hr and total FD fan air flows were between 1000-1100 Klb/hr.

Excess Oxygen. The target boiler O_2 level set prior to the test program was $3.8\% \pm 0.5\%$, which matches the target oxygen level set during the baseline test program in May 1994.

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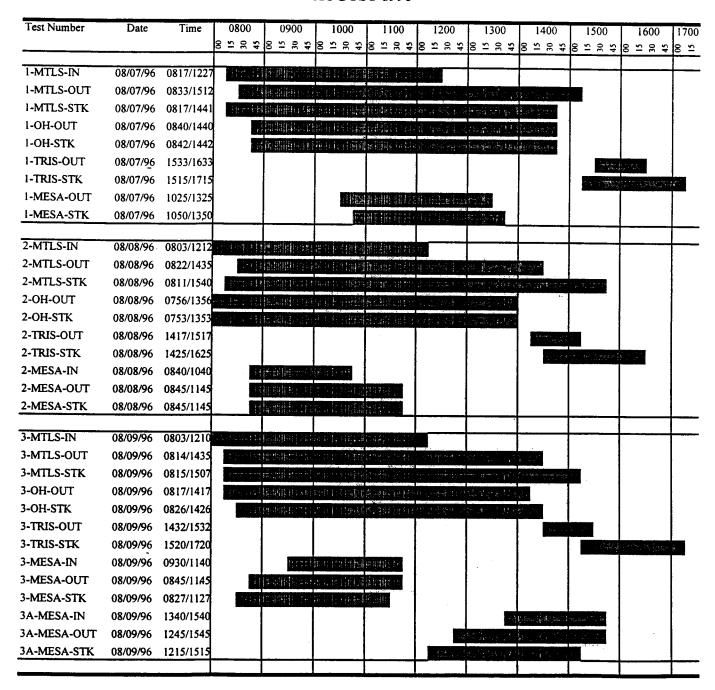
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TABLE 2-4
TEST SCHEDULE FOR MERCURY SPECIATION TESTING
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996



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NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM UNIT OPERATING CONDITIONS SUMMARY TABLE 2-5

AUGUST 1996

	1	ı	_	1									
		NOx	ppm (raw			182.2	194.3	203.1			231.0	228.8	0.077
	FGD Outlet/Stack	SO_{2}	Rem. Eff.			%8.68	%6.68	%616			95 6%	93 36%	0.1 20%
EMS	FGD Ou	SO ₂ ,	lb/hr			509.3	502.92	424.83			363.67	325.15	21.790
Plant CEMS		SO ₂ ,	ppm (raw) lb/hr Rem Eff. ppm (raw			129.4	126.7	107.2					8 89
	nlet	SO ₂ ,	ID/IIL	,		5,012	4,989	5,214			4,913	4,853	4.674
	FGD Inlet	SO ₂ ,	ppin (raw)			1,573	1,556	1,605			1,588	1,540	1,506
	,	Opacity %	- 1			5.81	5.74	2.91			08 9	4 99	6.17
		Boiler O. %	? 5			3.30	3.29	3.28		,	7.85	2.89	2.76
.s. °F	Air.	inlet Outlet 0. %				<u> </u>	667	667		ò	067	298	297
Temperatures,	Air-	inlet				00 5	700	9		057	600	600	658
Tem	Main	Steam			700	5 6	200,1			300	00,	<u>.</u>	500,
Coat	Flow	Ib/hr ⁽¹⁾			114 905	120,001	120,122	(71,121		122.620	070,771	120,338	127,694
Total Air	(Fans A/R)	Klb/hr			1 088	104	<u> </u>			1.039	9301	000.	1,048
Readwater					1 044	1 042	1.036			040	101	7.0	1,04
Main	Flow	Klb/hr			1 098	1.105	1.099			1.092	1 081		3
Ž	Output, Output, Flow.	MW			148.9	149.6	149.1			147.7	1467	707	12.0
Gross	Output,	MM			158.6	159.4	158.8			157.5 147.7	156.6	1 58 9	0.00
Time				riod:	0800/1800	0800/1800	8/9/96 0800/1700, 158.8 149.1		od:	8/12/96 0800/1400 1	1400/2000	0800/1900	200
Date				c Test Pe	96/1/8	96/8/8	96/6/8		Test Peri	8/12/96	3/12/96	96/1/2	
Test	Period			Inorganic Test Period:	_	7	m		Organic Test Period:	7	S	90	,

(1) Calculated from Carnot pitot flow rate data and EPA Method 19 F-Factor (reported on an as-received basis)

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Excess O_2 levels measured during the inorganic test period were steady at the low end of this target range averaging 3.3% each day. For the organic test period, however, Unit 2 was operated at a lower excess oxygen level averaging 2.8%. The reason for 0.5% lower excess O_2 during the second portion of the test program was not made clear to Carnot. May 1994's excess oxygen levels produced only a minimum amount of CO (8-11 ppm). The somewhat higher CO levels expected to be associated with 0.5% lower excess oxygen are not believed to have had a significant impact on hazardous organic emissions.

Sootblowing. Each morning after the unit load was stabilized and prior to the commencement of sampling, sootblowing was performed. During testing the normal sootblowing schedule was adhered to. Sootblowing schedules for this test program can be found in Appendix C.1.

ESP Operation. Unit 2's ESPs were operated at their peak efficiency with all fields in service. ESP power levels are documented in Appendix C.1.

FGD Operation. FGD SO₂ removal rate was maintained within the target range of 90-95% for the test program. The major process systems of the FGD were operated normally.

Unit operation was documented using plant instrumentation data logs. Data from Unit 2's CEM systems located at the ESP outlet/FGD inlet (SO_2 , CO and opacity) and FGD outlet/stack (NO_x , SO_2 , and CO_2) were also documented. Plant CO_2 measurements were used by Carnot for emission calculations. Unit operating data logs can be found in Appendix C.1. Unit CEMS data can be found in Appendix C.2.

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SECTION 3.0

SAMPLING AND ANALYTICAL METHODS

This section describes the sampling methods that were used for flue gas tests at the ESP inlet, ESP outlet and stack locations followed by descriptions of the analytical techniques used for all process stream samples. Section 3.3 discusses sample handling and preservation procedures for this test program. Section 3.4 explains how non-detected values, reagent blanks, field blanks, and uncertainty calculations were handled.

3.1 SAMPLE TRAINS

Table 3-1 lists the eleven sample trains that were used to conduct the flue gas sampling portion of the test program. The following sections explain each test method in more detail. Table 3-2 summarizes the sample train configurations including train materials and impinger contents. For the remainder of this report, "front-half" of the sample train refers to the section of train before and including the filter and any recovery portions from that section, and "back-half" refers to all train components and their recovery rinses downstream of the filter.

A "Method 5" style out-of-stack filtration sampling train was used at all locations. Borosilicate glass nozzles, probes, and filter holders were used for most tests. Six-foot probes were used at the ESP inlet and outlet locations for full traverse tests. Four-foot probes were used for single-point tests. At the stack, 12 foot probes were used for full traverse tests and 4 foot probes for single-point tests. Teflon sample lines were used to connect the back of the filter holder to the impingers.

3.1.1 Multi-Metals

The back-half of the EPA Method 29 sample train used to collect volatile metals that passed through the nozzle/probe and filter consisted of a Teflon sample line followed by a series of six ice-water chilled impingers. Following an empty stub-stem impinger for moisture removal, the next two impingers contained a 5% nitric acid/10% hydrogen peroxide solution, followed by an empty "middle knockout" impinger to prevent the permanganate solution in the fifth impinger from contaminating the nitric acid impingers. The fifth and sixth impingers contained an acidified potassium permanganate solution to collect any mercury that was not removed by the nitric acid impingers.

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TABLE 3-1 TEST PROCEDURES FOR AIR STREAM SAMPLES NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

Sample Train	Sampling Method	Species Measured	Isokinetic/ Constant Flow Rate	Test Duration*	Traverse Points
Inorganic Test Period				· · · · · · · · · · · · · · · · · · ·	
1) Multi-Metals	EPA Method 29	Note ⁽¹⁾	Isokinetic	A1: 240 A2,A3: 360	Full Traverse
2) Total Particulate/ Anions	EPA 5/8 CARB 421	Particulate, Cl ⁻ , F, SO ₄ ²	Isokinetic	A1: 120,240 A2,A3: 240	Full Traverse
3) Frontier Geosciences	MESA	Hg(0), Hg(II), Total Hg	Constant Flow Rate	A1: 120 A2,A3: 180	A1,A2: Multi-Point ⁽²⁾⁽³⁾ A3: Single Point
4) Ontario-Hydro	Ontario-Hydro Hg Spec. Train	Hg(0), Hg(II), Total Hg	Isokinetic	A2,A3: 360	Single Point ⁽²⁾
5) TRIS Buffer	TRIS Buffer Hg Spec. Train	Hg(0), Hg(II), Total Hg	Isokinetic	A2: 60 A3: 120	Single Point ⁽²⁾
6) Sulfur Oxides	Controlled Condensate, EPA Method 8	SO ₃ , SO ₂	A2: Constant Flow Rate A3: Isokinetic	60,90	A2: Single Point ⁽²⁾ A3: Full Traverse
7) Particle Sizing	Cascade Impactor	sub-10 micron PM	Constant Flow Rate	60	Multi-Point(2)(3)
Organic Test Period					
3) Semi-Volatile Organics	CARB 429	PCDD/PCDF PAH	Isokinetic	240	Full Traverse
9) Hexavalent Chromium	EPA Recirculation Method	Cr ⁶⁺	Isokinetic	A1: 120 A3: 180	A1: Full Traverse A3: Single Point
0) Formaldehyde	EPA 0011 (full-sized impingers)	Formaldehyde	Isokinetic	120	Full Traverse
1) VOST	EPA 0030	Benzene, Toluene	Constant Flow Rate	20 min/pr 4pr/test	Single Point

junction with each isokinetic test, velocity and maisture measurements were made according to EPA Methods 2 and 4.

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^{*} Key: A1 = ESP Inlet, A2 = ESP Outlet, A3 = Stack

⁽¹⁾ Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Ti, and V.

⁽²⁾ Replicates alternated ducts concurrently with opposite ESP location (if applicable).

⁽³⁾ Each replicate traversed entire sample port.

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NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM FLUE GAS SAMPLE TRAIN CONFIGURATIONS

				Out-of-Stack			Imi	mpinger Contents	S)	
Sample Train	Nozzle	Probe	Filter	Filter Holder	Sample Line	#1	#2	#3	#4	#3
BPA Multi. Metals	BSG	BSG L	110 mm Ukrapura quartz fiber	Method 5 BSG, Teflon frit	Teflon	Empty. stub stem	stem 100 ml 5% HNO 108 H,O.	100 ml 5% HNO/10% H ₂ O ₂	#5: 100 ml 4%. KMnO /10% H,SO.	#6; 100 ml 4% KMnO,/10% H,SO,
Hexavalent Chromium	3	Teflon with recirculating peristaltic pump teflon	N/A	N/A	Teflon w/ pH meter	200 ml 0.1 N KOH (Teflon- coated glass	75 mf 0.1 N KOH (Teflon)	75 ml 0.1 N KOH (Teflon)	Empty (Teflon)	#7:SG 300-400 g silica gel
Frontier Geoweience	NA COU	Quartz w/quartz wool	Two KCI/soda-lime traps followed-by twg todated carbon, traps	NIA.	Teflon, 1/8"	Impinger) Silica gel	*	N/A	Y'N	¥
Ontano-Hydro	BSG	BSG	110mm Ultrapure Quartz fiber	Method 5 BSG, Teflon frit	Teflon	#1, #2, #3: 100ml IM KCI	#4: 100ml 5% HNO ₃ / 10% H ₂ O ₂	#5: 100ml 5% HNO ₃ / 10% H ₂ O ₃	4 -	#9: 300-400g silica gel
TRIS	BSG BSG	BSG as a second	Ouarte fiber Ouarte fiber 110 mm Ultrapure	Method 5 BSG, STeffon frit Method 5 BSG, AL	Teflon	190ml 1M TRIST 150ml 1M 10mM BDTA TRISTIOMN 100 ml 100 ml	TRIS/10mM EDTA 100 ml	150ml 4% KMnO./ 10% H;SO.	~ ~ ~ ~ ~ ·	300-400g silica gel 300-400g
Anion Semi-VOST	BSG, 4	BSG - FEE	MeCly-Extracted	Method 5 BSG, A1,A2,Teflon-, coated, AL, frit, A3, Teflon frit, N/A	Teflon to XAD-2 resin column BSG	Empty-stub stem.	Natico, Na ₂ Co, 100 ml organic free DI H ₂ O	3% H ₁ O ₂ Empty	3% H,O, 300-400 g silica gel	N/A N/A
Formaldehyde, 1-	». BSG.	Teffon **	NA Quartz Thimble	, N/A BSG Thimble holder	15.00	100 ml DNPH 100 ml 3% H,O ₂	trap c 100 ml DNPH 100 ml 3%	coal cartridge Empty	trap 300-400g silica gel 300-400g silica gel	NA NA
Particle Sizing S. S. S. S. S. Key: Al = ESP inler NA = Not app	SST:	preseparators At a ESP outer SST = Staintess	G C C C C C C C C C C C C C C C C C C C	In-stack Cascade Inpactor A3 = Stack AL = Aluminum	wool, Teflon Teflon BSG = Borosili GF = Glass fiber	mi Di H ₂ O cate glass	100 ml E	Empty .	300-400g silica gel	NA

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Sample trains were pre-cleaned with concentrated HNO₃/HCl. One field blank for the ESP inlet/outlet location and one for the stack location were collected prior to the inorganic test period, and then two more field blanks (same locations) were collected at the end of the inorganic test period to compare with the "clean glass" field blanks.

3.1.2 Hexavalent Chromium

The method used for hexavalent chromium (Cr⁶⁺) sampling followed the procedures outlined in "Determination of Hexavalent Chromium Emissions from Stationary Sources" as part of the BIF regulations. Flue gas was sampled isokinetically across a full traverse of the ESP inlet location and at a single-point for the stack.

The key elements of the recirculation method are highlighted in Table 3-3. To eliminate the possibility of conversion of Cr^{6+} to Cr^{3+} between the nozzle and first impinger during testing, the Cr^{6+} collection reagent (0.1 N KOH) was continuously recirculated from the first impinger to the nozzle and back through the probe. The recirculating train is illustrated in Figure 3-1 and consisted of the following elements:

- borosilicate glass nozzle, teflon probe, teflon sample line, and pressure-side teflon tee
- teflon recirculation line, peristaltic pump, vacuum side teflon tee (for addition of 5 N KOH), and calibrated pH meter
- one teflon-coated glass impinger and two teflon impingers containing 0.1 N KOH for collection of Cr⁶⁺
- one empty teflon impinger
- one glass impinger containing silica gel.

A pH meter and a reservoir of 5 N KOH was connected to a teflon tee in the recirculation line to continuously monitor and adjust the pH of the collection reagent to >8. The first impinger was teflon-coated glass to provide better condensate removal (better heat transfer than teflon), and more volume (to prevent carryover).

3.1.3 Frontier Geoscience

Frontier Geoscience's mercury speciation absorption (MESA) sampling train selected for this test program is based generally on the sampling train and analytical procedures outlined in



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TABLE 3-3 HEXAVALENT CHROMIUM MEASUREMENT TECHNIQUES NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

Method EPA Recirculation Method (BIF regulations)

Train configuration Recirculation of Potassium Hydroxide solution (5 N KOH added

to recirculation fluid to maintain pH > 8)

Impinger material Teflon and borosilicate glass

Impinger contents 0.1 N KOH (Impingers 1-3)

Empty (Impinger 4)

Pre-test activities Pre-screen batches of 0.1N KOH and 5N KOH reagent solutions

for background levels of Cr⁶⁺. Discard batches containing >0.5 ppb. Pre-clean impinger trains with concentrated HNO₃/HCl.

Post-test activities 1. One-half hour nitrogen purge of sample train immediately

following sampling.

Nozzle through Impinger #4 rinsed with 0.1N KOH. 2. 3.

KOH impinger contents and 0.1N KOH rinse filtered through 0.8 µm cellulose ester filter after nitrogen purge.

Sample fractions Filtrate of KOH impinger contents and train rinse analyzed for

hexavalent chromium.

Blanks 0.1N and 5N KOH reagent blanks. No field blank required by

the method.

Analytical methodology:

Hexavalent Chromium Ion chromatography with Post Column Reaction (IC-PCR)

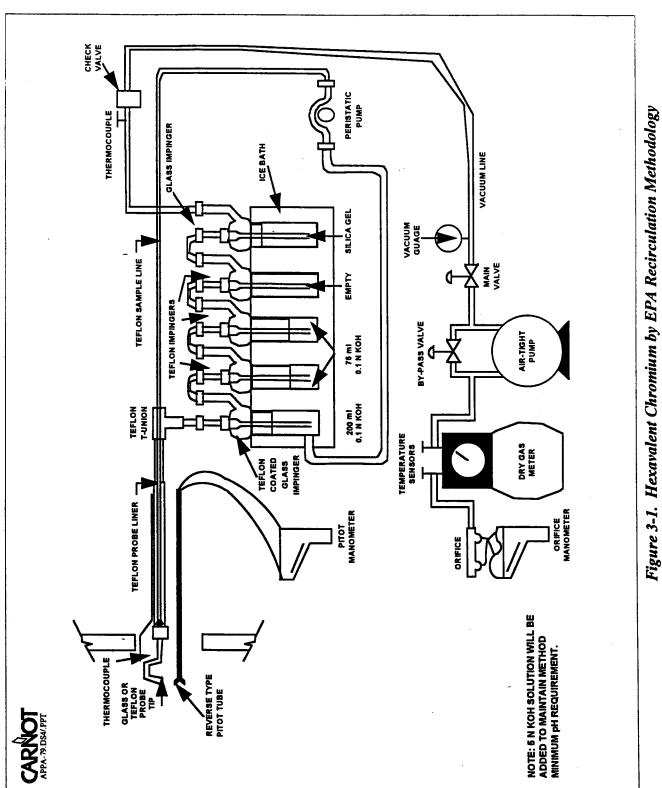
Cr6+ detection limit, µg/train 0.15

Specified maximum sample

Analyze for hexavalent chromium immediately after receipt at storage time

laboratory.

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the Analytical and Sampling Methods for Mercury Speciation in Flue Gases, Nicolas Bloom, February 1993. This sampling train consists of the following components.

- A quartz sample probe with quartz wool at the tip (to trap excess particulates). The probe pre-packed with wool is supplied and recovered by Frontier Geoscience.
- 2 pairs of tandem solid sorbent traps in series. The first pair of traps contains potassium chloride (KCl) impregnated soda lime granules. The second pair of traps contain iodated carbon.
- A section of Teflon tubing to connect the outlet of the final sorbent tube to a container of silica gel.
- A vacuum line to connect the outlet of the silica gel container to a control box.
- A control box containing a dry gas meter calibrated to 1-liter-per-minute, a sample pump, a temperature indicator and other components.

The quartz probe, with quartz wool and sorbent traps on opposite ends, was placed inside a borosilicate probe and heated to prevent moisture condensation prior to the traps. Non-isokinetic sampling was performed to determine only gas-phase mercury species. Sampling at the ESP inlet and outlet was performed within a single port at all three sample points. Single-point sampling was conducted at the stack.

No field blanks were collected. Two trip blank samples consisting of the probe with quartz wool and sorbent tubes were analyzed along with the samples.

3.1.4 Ontario-Hydro/TRIS Buffer Mercury Speciation

The Ontario-Hydro and TRIS Buffer sampling trains are modifications of EPA Method 29 with the only differences being the number and content of the impingers. For the Ontario-Hydro method, the first three impingers contain a potassium chloride (KCl) solution, the fourth and fifth impingers contain a 10% $\rm H_2O_2/5\%$ HNO₃ solution, and the last three impingers contain 4% KMnO₄/10% $\rm H_2SO_4$. For the TRIS Buffer technique, EPA 29's nitric acid/peroxide impinger contents are replaced with a tris(hydroxymethyl) aminomethane buffer solution. Ethylene di(tetraamine) or EDTA is added to the TRIS buffer solution as a complexing agent. Table 3-2 provides the exact sample train configurations for both methods.

Operation of the Ontario-Hydro and TRIS sampling trains followed EPA Method 29 sampling procedures. Both trains were operated at a single-point. The Ontario-Hydro sampling time was six hours to match EPA Method 29's. The TRIS Buffer train was operated for one hour at the ESP outlet and two hours at the stack in order to maintain the pH of the buffer above 6.5. The Ontario-Hydro and TRIS methods were performed simultaneously at both sampling locations and conducted in series.

Sample trains were pre-cleaned with concentrated HNO₂/HCl. For these sample trains no impinger glassware was used more than one time.

Daily field blanks and field blank spikes were taken at the ESP outlet location for each method.

3.1.5 Total Particulate/Anions

Flue gas was drawn isokinetically through a nozzle, probe and a tared quartz fiber filter heated to 250°F. At the ESP inlet, a cyclone separator located just before the filter was used to collect the large amounts of ash found at this location. Total filterable particulate was determined gravimetrically on the front-half of the sample train only as per EPA Method 5. Filters were oven-dried at 250°F and desiccated according to Method 5 before their initial weights were taken.

A series of five impingers were used for vapor phase anion collection according to a combined EPA 8/CARB 421 sampling method. The first two impingers contained a sodium carbonate/sodium bicarbonate solution, the third and fourth impingers contained 3% hydrogen peroxide, and the fifth had silica gel. The impinger contents were analyzed for chloride, fluoride, and sulfate. The front-half of the sample train was also analyzed for the anions for mass balance purposes.

A field blank was set-up, recovered, and analyzed along with the samples for both the ESP inlet/outlet and stack locations.

3.1.6 Semi-Volatile Organics

Consistent with the May 1994 Unit 2 baseline test program, all semi-volatile species were collected and analyzed from a single CARB 429 sample train. Appropriate standard spiking sequences, sample recovery, and soxhlet extractions steps were added to ensure that PCDD/PCDF analyses could be conducted according to EPA Method 23 and that PAH analyses could be performed according to CARB 429. Table 3-4 summarizes the pertinent information for this test.

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TABLE 3-4 SEMI-VOST TEST INFORMATION NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

Sampling Method

CARB 429 - August, 1992 (revised draft)

Analytical Method

CARB 429: HRGC/LRMS with SIM for PAH

EPA 23: HRGC/HRMS for PCDD/PCDF

Analytical Laboratory

Zenon Environmental Laboratories

Achieved Detection Levels

PAH: 0.003-0.08 μg/Nm³ (per species)

PCDD/PCDF: 0.0005-0.004 ng/Nm³ (per substituted isomer)

Sample Volumes Standards Spiking ESP Inlet: 3.4 Nm³, ESP Outlet: 3.6 Nm³, Stack: 3.9 Nm³

Field surrogates, internal spikes, and recovery spikes of isotopically labeled standards were added prior to sampling, extraction, and analysis, respectively, as per CARB 429 and EPA 23 by Zenon

Environmental.

Blank

Full field blank train assembled, recovered and analyzed.

Recovery

Filters stored in organic-free amber glass jars with Teflon lined lids at =4°C. XAD-2 column with ends capped and wrapped to protect

from light stored at \approx 4°C.

Front-half glassware including sample line rinsed 3 times each with laboratory GC-grade acetone, hexane and methylene chloride. A final toluene proof-rinse is stored as a separate fraction. The first three impinger contents are recovered and stored separately. A triple rinse of the first three impingers with acetone, hexane, methylene chloride, and toluene are combined with their respective organic rinse fractions. Organic and water fractions, including the toluene proof-rinse, stored in organic-free amber glass bottles and stored at \approx 4°C.

All sample fractions shipped cold (~4°C).

Fractions Analyzed

The organic fraction, filter, sorbent module and water fraction are combined and split for CARB 429 analysis. The toluene proof-rinse

is added to one split and analyzed by EPA 23.

Chain of Custody

Maintained by Carnot and Zenon on all samples.

Glassware Cleaning

Thorough cleaning, followed by DI H₂O, acetone, toluene and methylene chloride rinses, followed by high temperature bake.

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Samples were collected isokinetically and passed through a heated EPA Method 5-type methylene chloride-extracted Teflon filter followed by a water-cooled condenser and a sorbent module containing approximately 40 grams of 30/60 mesh Amberlite XAD-2 resin (pre-extracted). The sorbent module is followed by an impinger train to collect moisture and any species that might pass through the resin. An unheated teflon sample line was used to connect the filter holder outlet to the condenser inlet. One field blank for the ESP inlet/outlet location and one for the stack were set-up, recovered, and analyzed along with the samples.

3.1.7 Volatile Organic Compounds

Benzene and toluene levels in the flue gas stream were determined by VOST according to EPA Method_0030. The sampling train illustrated in Figure 3-2 consists of a heated borosilicate probe containing a glass wool filter and connected to an adsorption cartridge containing 1.6 grams of Tenax-GC followed by a condensate trap. A borosilicate section of tubing connects the outlet of the condensate trap to a back-up sorbent trap containing 1 gram of Tenax-GC and 1 gram of activated charcoal followed by a second condensate trap. Sampling was performed at a single point.

A sample run consisted of collecting four VOST tube pairs each for a 20-minute period. The sampling rate was approximately 1.0 liter per minute. To minimize the potential for solvent contamination, preparation and recovery of the VOST test trains were performed at the sample locations isolated from the laboratory activities of the other test trains. Two field blank trains per location, one prior to testing and one after, were set-up, recovered and analyzed with the samples. The tenax-GC resin was pre-screened in batches of 10 to ensure low background levels of benzene and toluene.

3.1.8 Formaldehyde

Flue gas concentration levels of formaldehyde were determined by EPA Method 0011. Flue gas was collected isokinetically through a borosilicate glass nozzle and a teflon probe/sample line into a pair of chilled impingers containing 100 ml of DNPH. A full traverse of the ESP outlet and stack locations were performed. A blank train per location was set-up, recovered and analyzed along with the samples as a field contamination check.

3.1.9 Sulfur Oxides

Sulfur oxides present in the flue gas stream were measured using EPA's controlled condensate method developed by TRW. A metered gas sample was drawn at a rate of 0.8 cubic feet per minute through a heated borosilicate probe, a heated quartz thimble filter, a temperature-controlled borosilicate coil and quartz wool plug for sulfuric acid mist (SO₃) collection, followed by two impingers containing 3% H₂O₂ for collection of SO₂.

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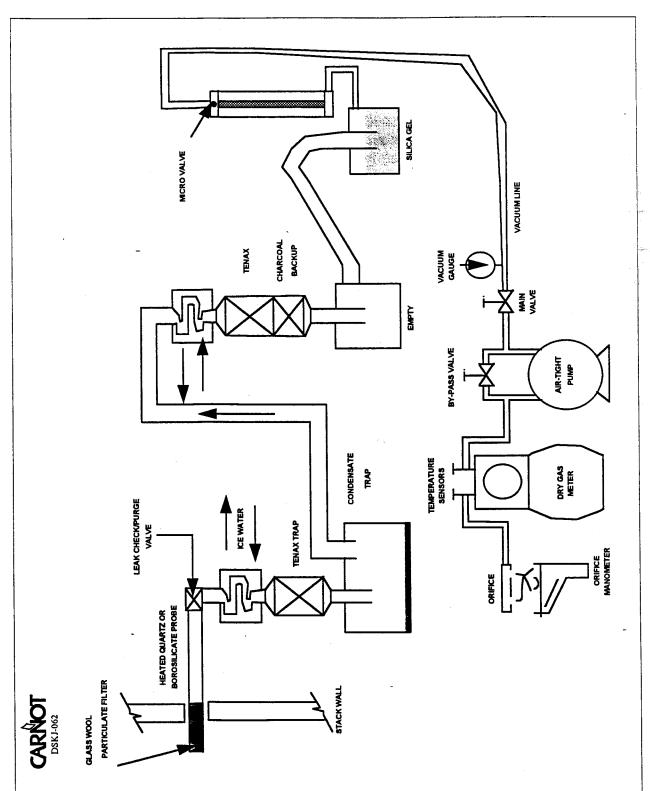


Figure 3-2. EPA Method 0030 - Volatile Organic Sampling Train (VOST) (NYS-10 WMF)

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The probe and filter are heated to $550^{\circ}F$ to remove particulate matter but not SO_3 which will pass through as a vapor at that temperature. SO_3 is collected in the borosilicate coil followed by a quartz wool plug heated together to $160\pm10^{\circ}F$ which is below the sulfuric acid dew point but above the moisture dew point. These temperatures will allow SO_2 to pass through the entire sample train until it reaches the peroxide impingers. No field blank was taken.

At the ESP outlet, SO₃ exists in the gas phase because flue gas temperatures are above the sulfuric acid dew point. Therefore tests at this location were single point, non-isokinetic. At the stack, SO₃ exists as sulfuric acid mist, so samples were collected isokinetically across a full traverse. The use of a SO₃ condensation sampling method at a condensing stack location does present some concerns regarding a possible high bias associated with its measurement of SO₃ by counting sulfates contained in the scrubber mist carryover liquid collected by the sample train as sulfuric acid mist. By maintaining the probe and filter at 550°F it is hoped that any scrubber mist carryover collected by the sample train will be evaporated/filtered and any sulfates will be liberated as SO₂ and not SO₃.

3.1.10 Particle Size Distribution

A three-point flue gas sample was withdrawn from a single ESP outlet port isokinetically so that particles in the gas stream are inertially separated onto a series of impactor stages. Particulate concentration on eight size cuts from 0.3 to 10 microns was determined gravimetrically. The impactor was a University of Washington, Mark III cascade impactor.

The cascade impactor assembly includes a nozzle and a right-angle preseparator followed by the impactor body. Inside the impactor body are seven separation stages containing tared collection filters followed by a tared back-up filter. The impactor was located inside the duct so that sampling is at flue gas temperatures. A teflon sample line connected the impactor body to a standard EPA Method-5 type control box.

Sample flow rates and nozzle sizes were selected to achieve both isokinetic sampling between 90-110% and a target particulate cut size between 9-11 microns in the preseparator. Particle cut-off size is a function of preseparator and impactor stage design, sample gas viscosity and temperature, and sample flow rate. The average cut-off size determined from manufacturer's calibration curves for the three sample runs performed was 10.7 microns.

After completing the first 60-minute impactor test run, a visual inspection of the collection stages determined that although the run was valid, a 90-minute test time for the remaining two runs would be more appropriate. Sample run lengths collected 0.3 to 1.3 milligrams of particulate per collection stage. No field blank was taken.

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3.1.11 Semtech Hg 2000 Analyzer

EERC provided a Semtech Hg 2000 instrumental analyzer manufactured by Semtech Metallurgy AB, Lund, Sweden for use at the stack location. The analyzer measures Hg(0) on a real-time continuous basis using a Zeeman-shifted ultraviolet sensor. The Semtech's Zeeman-shifted detection technology eliminates interference from SO_2 absorption.

A heated glass probe, a teflon sample line, and two ice water-chilled TRIS impingers were used to provide dry, Hg(II)-free conditioned flue gas to the analyzer. The Semtech was auto-zeroed and zero-checked on ambient air daily. No span calibrations can be performed on this analyzer. (It is uncertain whether the manufacturer will develop a spanning method for this analyzer.) The flow rate to the analyzer was set at approximately 3 L/min and data was logged in 1 minute intervals. Ambient air was used to purge the analyzer between test days. The analyzer was operated each day of the inorganic test period and instrument readings in ug/dscm were averaged over time intervals that corresponded to stack Ontario-Hydro and TRIS Buffer sampling periods.

The Semtech was also operated at the ESP outlet during the second-half of Day 3 (TRIS Buffer sampling period) of the inorganic test period, and for part of the following day; however, the instrument readings are considered unreliable and the results were deemed invalid due to the use of an improper sample conditioning system and detrimental ambient conditions (i.e. high temperature and dust level). For sampling at the ESP outlet (where flue gas temperatures were near 300°F) it would have been more appropriate to use a heated transfer line between the heated sampling probe and the chilled impingers to prevent Hg(II) deposition in the transfer line. It is not well understood but the deposition of Hg(II) on analyzer surfaces located prior to the detection and quantification of Hg(0) can cause interferences. Furthermore, a longer sampling probe should have been used due to the highly negative duct pressure (-14 to -15 iwg). The ambient temperature at the ESP outlet during sampling was around 120°F which was well beyond the instrument's recommended operating temperature range of 41°F to 95°F. Operation of the analyzer at this elevated temperature level overheated the power supply. Finally, the design of the analyzer does not include a sealed optical path, and the analyzer uses ambient air for ventilation. The ambient air at the ESP outlet contained a high level of dust-which may have settled on the lamp and/or cell window surfaces interfering with the optical path of the Hg(0) detection system.

3.1.12 Diluent Gases

To determine the O_2 levels at each sample location and the integrity of each isokinetic, multi-point test train, a Teledyne portable O_2 analyzer using a paramagnetic cell sampled conditioned flue gas from the outlet of the calibrated orifice on each control box at every sample

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point. The portable O_2 analyzer's linearity was verified daily using EPA Protocol 1 certified gas standards.

For emission rate calculations, CO_2 levels at the stack were averaged from NYSEG's CEM system for corresponding stack test periods, and then corrected to ESP inlet and outlet test period O_2 values.

3.1.13 Flue Gas Velocity and Moisture

Flue gas velocity, moisture and flow rate determinations were performed according to EPA Methods 2 and 4 in conjunction with every full traverse isokinetic test. For single point tests (i.e. chromium speciation, Frontier Geoscience, Ontario-Hydro, TRIS Buffer, VOST, sulfur oxides, and particle sizing) flow rates for mass emission calculations were taken from corresponding full traverse isokinetic tests.

3.2 ANALYTICAL METHODS

Tables 3-5 and 3-6 present a summary of the analytical methods used on the NYSEG Milliken Unit 2 post-retrofit chemical assessment program. The following sections discuss each analytical method employed on this project in detail. Flow charts are presented in appropriate sections when complex analytical procedures for multi-fraction samples require illustration. Any problems associated with the sample analyses are also discussed in appropriate sections.

3.2.1 <u>Trace/Major Elements</u>

EPA Method 29 samples were recovered into the following fractions:

- 1) Particulate filter Container No. 1
- 2) Front-half fraction
 - 2a) Acetone rinse and brush Container No. 2 (ESP inlet samples only)
 - 2b) Nitric acid rinse Container No. 3
- 3) Back-half empty and nitric acid/peroxide impingers/rinse Container No. 4
- 4) Nitric acid rinse of middle knockout impinger Container No. 5A
- 5) Potassium permanganate/sulfuric acid impingers/rinses Container No. 5B
- 6) Hydrochloric acid rinse of permanganate impingers Container No. 5C (combined with Container No. 5B at laboratory).

Analytical procedures used for trace element determination were in accordance with EPA Method 29 as illustrated in Figure 3-3. Although not specified in the method, major ash elements

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TABLE 3-5 ANALYTICAL PROCEDURES FOR AIR STREAM SAMPLES NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

Sample Train	Analytical Reference Method	Measurement Principle	e Laboratory	Method Detection Limits	Target Sample Rate	Comments
Trace/Major Elements(1):			Zenon	ug/Nm³	l m³/hr	Front-Half/Back-Half
Antimony	EPA 7041/6020	GFAA/ICP-MS		0.10	1 111 /111	Combined,
Arsenic	EPA 7061/7060	HGAA/GFAA		0.10		
Barium	EPA 6010	ICP-AES		0.05		Four Train Fractions fo
Beryllium	EPA 6010/7091	ICP-AES/GFAA		0.01		Hg
Cadmium	EPA 7131	GFAA		0.005		
Chromium	EPA 6010	ICP-AES		0,20		
· Cobalt	EPA 6010/7201/6020	ICP/GFAA/ICP-MS		0.10		
Copper -	- EPA 6010	ICP-AES		0.30		
Lead	EPA 7421	GFAA		0.05		
Manganese	EPA 6010	ICP-AES		0.30		
Mercury	EPA 7471	CVAAS		0.01		
Molybdenum	EPA 6010/7481	ICP-AES/GFAA		0.50		
Nickel	EPA 6010/7521	ICP-AES/GFAA		0.05		
Phosphorus	EPA 6010	ICP-AES		3		
Selenium	EPA 7741/7740	HGAA/GFAA		0.10		
Vanadium	EPA 6010	ICP-AES		0.20		
Hexavalent Chromium: Cr ⁶⁺	EPA Recirc. Method	IC/PCR	RTI	ug/Nm³ 0.05-0.08	1 m³/hr	ESP Inlet/Stack only
Frontier Geoscience:	MESA		Frontier Geoscience	ug/Nm³	0.4-0.5 L/min	
Hg (0)		DGA/CVAFS		0.05	0 0.5 <u>Dian</u>	
Hg (II)		DGA/CVAFS		0.01		
Total Hg		DGA/CVAFS		0.001		
Ontario-Hydro:	Ontario-Hydro Method		EERC	ug/Nm³	lm³/hr	ESP outlet/stack only
Hg (0)		CVAAS		0.10		-or ouncommen only
Hg (II)		CVAAS		0.01		
Total Hg		CVAAS		0.001		
TRIS	TRIS Buffer Method		EERC	ug/Nm³	1m³/hr	ESP outlet/stack only
Hg (0)		CVAAS		0.10		
Hg (II)		CVAAS		0.01		
Total Hg		CVAAS		0.001		
otal Particulate/Anions:			Zenon		1 m³/hr	
Particulate	EPA 5	Gravimetric		0.0002 gr/dscf		Solid PM only
Chloride	EPA 9056	Ion Chromatography		0.003 ppm		Both Solid and Vapor
Sulfate	EPA 9056	Ion Chromatography		0.15 ppm		Both Solid and Vapor
Fluoride	EPA 13B	Ion Selective Electrode		0.01 ppm		Both Solid and Vapor
article Sizing:	Cascade Impactor	Gravimetric	Carnot	0.0002 gr/dscf	1 m³/hr	ESP outlet only
emi-Volatile Organics:		•	Zenon		l m³/hr	•
PAH PCDD/PCDF	CARB 429 EPA Method 23	HRGC/LRMS-SIM		0.003-0.08 ug/Nm ³		
Formaldehyde:	EPA 0011A	HRGC/HRMS		0.0005-0.004 ng/Nm ³		
OST:		HPLC	Zenon	0.4 ppb	l m³/hr	ESP outlet/Stack only
Benzene, Toluene	EPA 5030/5040/8260	GC/MS	Zenon	0.07 ppb	1.0 L/min	ESP outlet/Stack only
Sulfur Oxides: SO ₂ , SO ₃	EPA Method 8	D				
50 ₂ , 30 ₃	EFA MEIROG 8	Barium Chloride Titration	Carnot	0.15 ppm	1 m³/hr	ESP outlet/Stack only
Molecular Weight (O2, CO2)	EPA Method 3A	Elect. Cell/NDIR	Carnot/Plant CEM	0.1%		Stack CEM
lue Gas Velocity, Moisture	EPA Methods 2.4	Pressure/Weight Diff.		with each test (excep		SIMUL CENT

Notes: (1) The major elements of Al, Ca, Fe, K, Mg, Na, Si, and Ti were also analyzed from the EPA Method 29 sample train using ICP-AES

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NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM SUMMARY OF ANALYTICAL METHODS SOLID STREAM SAMPLES TABLE 3-6

Process Stream	Trace Metals (including mercury)	Major Elements	Antimony (Coal Only)	Fluorine (Coal Only)	Fluorine (Ash, FGD Solids)	Chlorine	Sulfur
Solid Samples ⁽¹⁾⁽²⁾							
Ashing Method	EPA SW846-3051 microwave- assisted acid digestion	750°C as per ASTM D3682-78 ⁽³⁾	500°C as per ASTM D3683-78 ⁽³⁾	Tube furnace, 1150°C	1350°C, Oxygen Stream as per ASTM D3761-84	1350°C, Oxygen Stream as per ASTM D4208-83	Tube fumace, 1350°C
Digestion Method/ Collection Method	Closed pressure H ₂ SO ₄ /HNO ₃ digestion (coal only); closed pressure HNO ₃ , HF, HCl digestion (ash, FGD solids)	Open pressure HNO,, HF, HCI digestion	Open pressure Pyrohydrolysis Gasebus HF HNO3, HF, HCl using a weak- collected in digestion base scrubber dilute base solution	Pyrohydrolysis using a weak- base scrubber solution	Gasebus HF collected in dilute base solution	Gaseous HCl collected in dilute base solution	Analysis of gaseous SO ₂
Measurement Principle	ICP-AES; GFAA (for Sb, As, Cd, Pb in the ash only); CVAAS (for Hg); HGAAS (tor Se)	ICP-AES	GFAA	ISE	ISE	ISE	IR Absorption (instrumental)

N/A - Not applicable

(1) Solid samples were collected from their respective process streams according to ASTM D2234, and prepared for analysis according to ASTM D2013.
(2) Ultimate/Proximate Analysis performed on each solid sample as follows: Ultimate/Proximate Analysis performed on each solid sample as follows: Carbon, hydrogen, nitrogen:

ASTM D5373 (instrumental)
By difference
ASTM D5142-90 (instrumental)
ASTM D5142-90 (instrumental)
ASTM D1989-91

(3) Required for coal samples only. HHV (coal only):

Ash Content:

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were added to the list of trace elements required from the EPA 29 sample train in order to complete their material balance.

The front-half rinse is acidified with concentrated nitric acid to a pH of 2. Both the front-half and filter are decomposed separately using a nitric acid/hydrofluoric acid microwave digestion procedure to solubilize inorganic target elements and to remove organic constituents that may create analytical interferences. The empty and nitric acid containing impingers catch/rinse is acidified with concentrated HNO₃ to a pH of 2 then decomposed using a nitric acid/peroxide digestion. Aliquots of the decomposed probe wash, filter and nitric-acid impinger catch rinse are combined to achieve the lowest detection limits possible and analyzed for target elements by either graphite furnace atomic absorption (GFAA), hydride generation atomic absorption (HGAA), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), or inductively coupled plasma-mass spectrometry (ICP-MS) depending on method's detection limit and response to matrix interferences. Total sulfur was also analyzed from the EPA Method 29 samples by ICP-AES to confirm the levels found in the particulate/anion trains.

An aliquot of the combined front-half rinse and filter decomp along with an aliquot taken from the empty and nitric acid containing impinger catch/rinse are digested separately with nitric acid and permanganate and analyzed for mercury by cold vapor atomic absorption spectrophotometry (CVAAS). The middle knockout impinger rinse and the permanganate impinger catch/rinse are decomposed separately with nitric acid and permanganate and analyzed for mercury by CVAAS.

EPA Method 29 trace element results from previously sponsored EPRI and DOE toxic assessment programs for ESP/fabric filter inlet flue gas streams at coal-fired utility stations have shown poor agreement with fuel input and flyash levels. Method 29 attempts to digest the solids collected in the front-half of the sample train by dividing them into 0.5 gram portions and digesting them individually. This procedure becomes problematic when the quantity of ash collected exceeds 2-3 grams requiring over 5 separate digestions. Attempting and then combining more than 5 digests can not only introduce significant levels of contamination but any errors associated with solubilizing a single 0.5 gram portion are multiplied by the number of digests performed. For this test program, approximately 30 grams of solids were collected in the front-half of the ESP inlet sample trains. Digesting these sample train solids is further complicated when major ash elements are required. Oxides of silicon, aluminum and iron among others contribute 95-99% of Unit 2's flyash content creating a complex refractory matrix. These elements exist in a variety of compounds, a number of which are difficult to solubilize.

To address this problem of analyzing the ESP inlet samples and to be consistent with the May 1994 Unit 2 baseline test program, Method 29's recovery and analysis procedures were modified as illustrated in Figure 3-3 by asterisks. Instead of attempting to digest the entire

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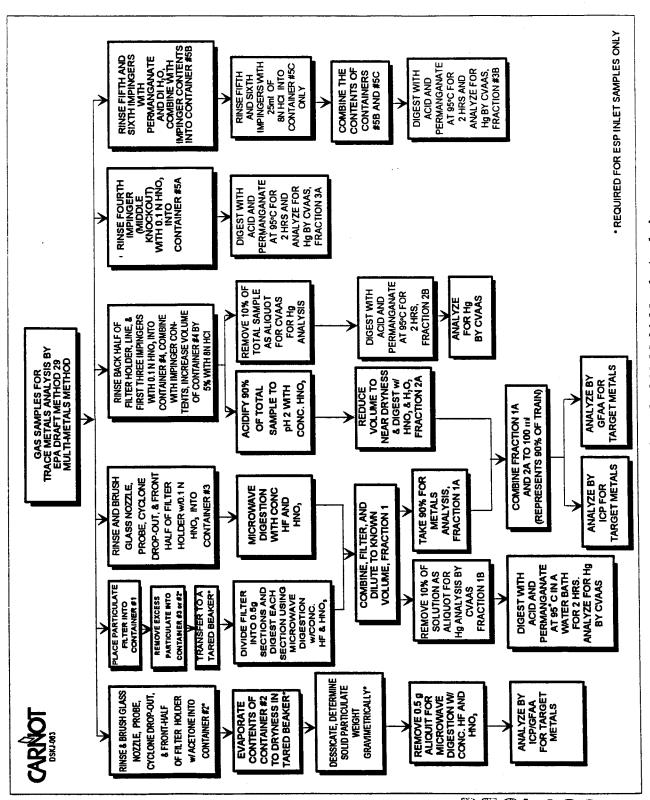


Figure 3-3. EPA Draft Method 29 Multi-Metals Analysis

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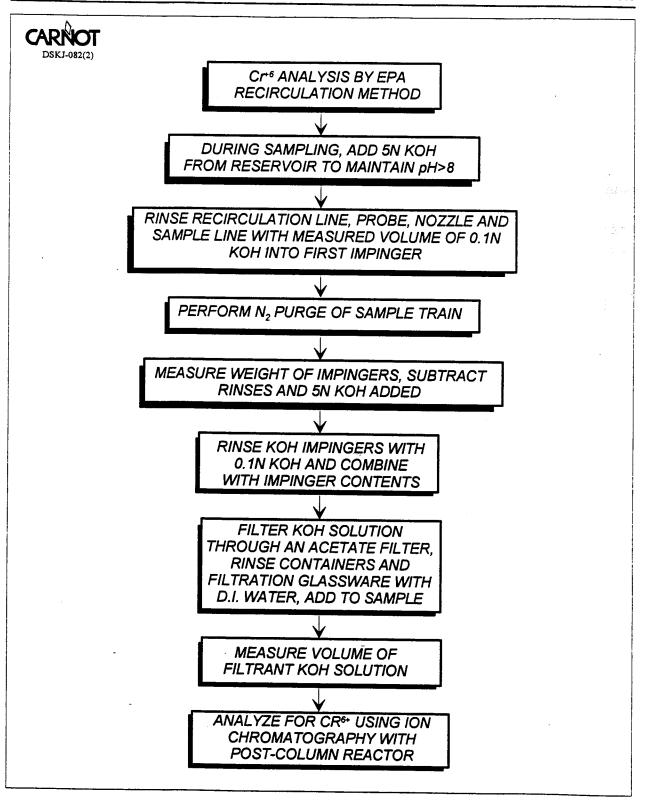


Figure 3-4. Hexavalent Chromium Analysis by the EPA Recirculation Method

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gold trap amalgamation and finally detected by CVAFS. The KCl/soda lime traps are first dissolved in a 5% (v/v) HNO₃/0.3 M citric acid solution. For the analysis of Hg(II) in the HNO₃/citrate digest, an additional 10 ml of HCl is added to the HNO₃:citrate digest to ensure all of the Hg(II) is in solution. Then aliquots of this digest are analyzed for Hg(II) by aqueous phase SnCl₂ reduction, dual gold trap amalgamation and finally detected by CVAFS. The analysis of the probe/wool recovery rinses for total Hg was accomplished by aqueous phase SnCl₂ reduction, dual gold amalgamation and CVAFS detection of appropriate sized aliquots.

All standards are ultimately traceable to the lab stock standard for total Hg supplied by the NIST (formerly NBS). Also, where possible, certified standard materials were analyzed along with the samples.

3.2.4 Ontario-Hydro/TRIS Buffer Mercury Speciation

EERC prepared, recovered, and performed the mercury speciation analysis of the Ontario-Hydro and TRIS Buffer sampling trains. Appendix A contains EERC's protocols for sample train recovery, sample preparation, and analysis procedures. It should be noted that along with Frontier Geoscience's method, the Ontario-Hydro and TRIS Buffer mercury speciation techniques are still under review and are not approved procedures at this time.

Samples collected using the Ontario-Hydro method were recovered into the following fractions as shown in Figure 3-5:

- 1) Particulate filter and ash Container No. 1
- 2) Front-half nitric acid rinse Container No. 2A
- Back-half nitric acid rinse and potassium chloride impingers and rinses (permanganate, hydrochloric acid, nitric acid) Container No. 2B (Container 2A was combined with 2B for analysis on the first replicate)
- 4) Nitric acid/peroxide impingers and rinses (nitric acid) Container No. 3
- 5) Permanganate/sulfuric acid impingers and rinses (hydrochloric and nitric acids) Container No. 4

Samples collected using the TRIS Buffer technique were recovered into the following fractions as shown in Figure 3-6:

- 1) Particulate filter and ash Container No. 1
- 2) Front-half nitric acid rinse Container No. 2A
- 3) Back-half nitric acid rinse and TRIS/EDTA impingers and rinses (TRIS, DI H₂0) Container No. 2B



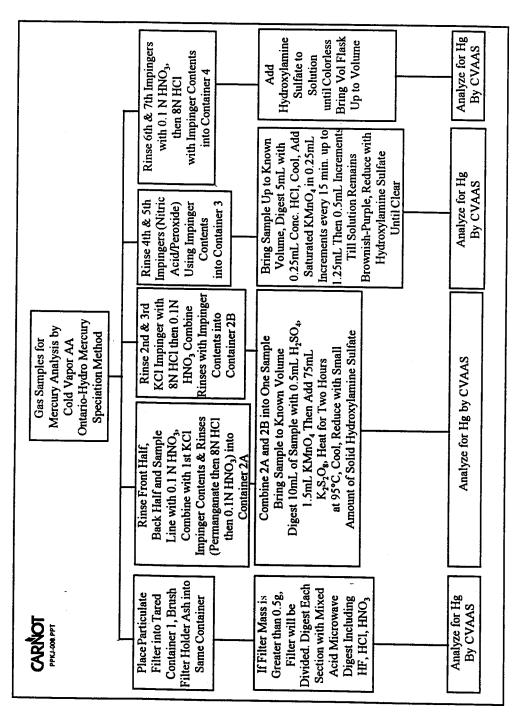


Figure 3-5. Ontario-Hydro Mercury Speciation Analysis

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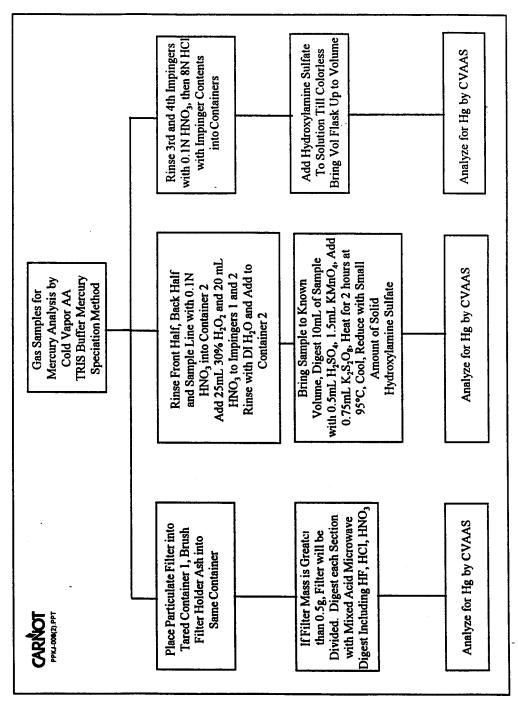


Figure 3-6. TRIS Buffer Mercury Speciation Analysis

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4) Permanganate/sulfuric acid impingers and rinses (hydrochloric and nitric acids) - Container No. 4

Potassium chloride sample fractions were immediately preserved with acidified potassium permanganate and then digested using a potassium persulfate digest procedure. Nitric acid/peroxide sample fractions were preserved with 10% HCl, then combined with potassium permanganate until solution remains purple. At this point, hydroxylamine sulfate was added until the solution becomes clear. TRIS/EDTA sample fractions are digested with potassium persulfate. Hydroxylamine sulfate is added to the potassium permanganate/sulfuric acid sample fractions until solution turns clear. All liquid sample fractions were then analyzed on-site for mercury by CVAAS.

The particulate filter fraction was HCl/HF microwave digested and analyzed at EERC's University of North Dakota laboratory.

For the Ontario-Hydro method, the KCl fraction results are reported as Hg(II), and the remaining fraction results are reported as Hg(0). For the TRIS Buffer technique, the TRIS/EDTA impinger results are reported as Hg(II), and the KMnO₄/H₂SO₄ impinger results are reported as Hg(0). Any mercury found on the filter is reported as total mercury. Any mercury found in the probe rinses for either method was considered Hg(II) for the following reasons:

- Mercury levels in the flyash were measured just under 0.1 ppm. At this
 concentration, significant levels of mercury adsorbed on the ash will not be found
 in the front-half portions of the FGD inlet and outlet sample trains since such
 small levels of flue gas particulate are collected.
- Mercury analyses of the filters from FGD inlet/outlet TRIS, Ontario-Hydro and EPA Method 29 sample trains found little or no mercury.

As a result, any significant levels of mercury found in the front-half rinse of the trains was assumed to be Hg(II) that deposited on the probe/filter holder surfaces due to the lower than optimal probe/filter temperatures of approximately 250°F. Hg(II) is much more likely to deposit on front-half glassware surfaces than Hg(0) at this temperature range.

Since daily field blanks and field blank spikes were taken no reagent blanks were analyzed.

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3.2.5 Total Particulate/Anions

Following completion of the test, the sample filter was quantitatively recovered and the front-half of the sample train was rinsed with acetone. The gravimetric particulate analysis on the front-half of the sample train was performed by Zenon using EPA Method 5. After evaporating the front-half acetone rinse in a tared beaker, the front-half rinse and filter are baked at 105°C, desiccated and weighed until a constant weight was found (less than 0.5mg difference between consecutive 6-hour weighings). Following the particulate analysis, the front-half rinse and filter fractions were soaked in DI H₂O, which was then filtered and analyzed for anions as shown in Figure 3-7.

The front-half rinse and filter fractions were analyzed along with the bicarbonate impinger fraction by ion chromatography (IC) with conductivity detection for Cl⁻ and SO₄²⁻ according to EPA Method 9056, and by ion-selective electrode (ISE) according to EPA Method 13B for fluoride using a distillation column to prepare the samples for analysis. The peaks for these species by IC analysis are identified by characteristic retention times and quantified by reference to external standards. Titrametric analytical techniques were employed for the determination of chloride and sulfate from the 3%H₂O₂ fraction. For chloride, a mercuric nitrate titration was performed according to EPA Method 325.3. The sample is acidified then titrated with mercuric nitrate in the presence of a mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex. The peroxide fraction was analyzed by EPA Method 8. Isopropyl alcohol is added to the sample before it is titrated with barium chloride in the presence of a modified thorin green indicator. The end point of the titration is the formation of the pink-grey barium sulfate complex. No breakthrough of fluoride past the bicarbonate impingers was expected.

A reagent blank for each of the four train fractions were taken in the field and analyzed along with the samples.

Based on fuel sulfur levels and plant SO₂ CEMS data, the sulfur results from this method were deemed invalid. The low levels of sulfur found in these sample trains were most likely due to an "over-saturation" of the peroxide impingers. A more concentrated peroxide solution should have been used given the sample time and SO₂ levels expected. In addition, the water leaching of the sample train's front-half did not appear to completely solubilize all sulfur species. EPA Method 29 total sulfur results and flyash sulfur concentration levels were used in place of these data, their differences providing gaseous sulfur values.

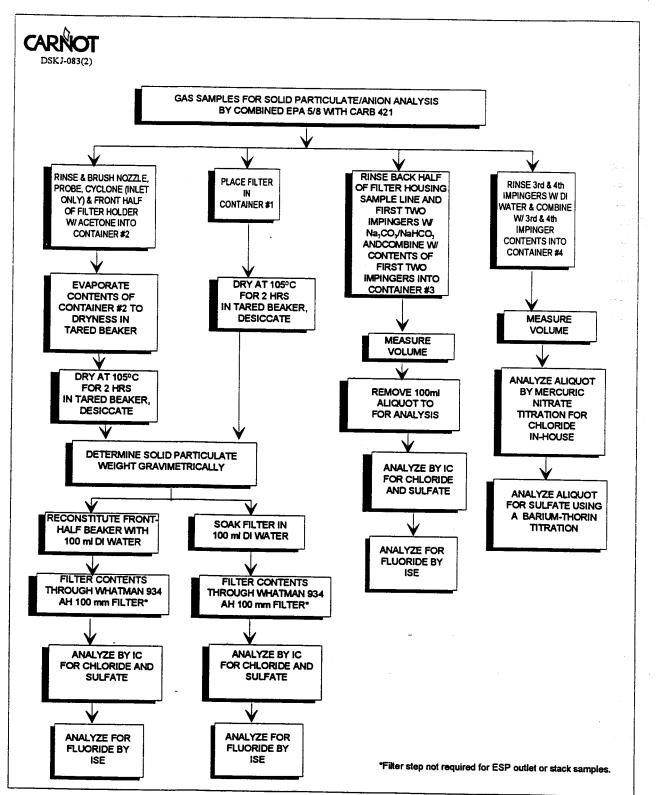


Figure 3-7. Solid Particulate/Anion Analysis DECLASSIFIED

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3.2.6 <u>Semi-Volatile Organics</u>

Sample analyses were performed by Zenon Environmental Laboratories as illustrated in Figure 3-8. Zenon prepared the resin, loaded the modules, and extracted the modules and other fractions according to CARB 429 and EPA 23 procedures. Appropriate field surrogate standards as required by the methods were introduced to the XAD-2 resin prior to sampling. The PAH and PCDD/PCDF analytical methods add isotopically labeled internal standards to the samples prior to organic extraction to quantitate PAH and PCDD/PCDF species through recovery corrections. Both analytical methods specify matrix-specific extractions of the samples with appropriate organic solvents, and preliminary fractionation and clean-up of extracts depending on analyte-type. The percent recoveries of the (pre-sampling) field surrogates and (pre-extraction) internal standard spikes were reported along with the recovery corrected sample results. Two isotopically labeled PCDD/PCDF recovery standards, 1,2,3,4 TCDD and 1,2,3,7,8,9 HxCDD, were added to the samples prior to analysis as per EPA Method 23 to correct for variations in injection volumes. The toluene proof-rinse was kept separate from the other organic rinses since toluene is believed to interfere with the PAH analysis.

After concentrating the organic rinse fractions (except toluene) and adding internal standards to the resin and filter fractions, they were combined and soxhlet extracted with methylene chloride. The process extract was split and one portion was combined with the water fraction, after a separator funnel methylene chloride liquid/liquid extraction, and concentrated and cleaned-up for PAH analysis by high-resolution capillary column gas chromatography (HRGC) with low-resolution mass spectrometry (LRMS) in selected ion-monitoring (SIM) mode. The other methylene chloride process extract was combined with a second soxhlet extraction with toluene and the toluene rinse fraction, after internal standards were added, cleaned-up, and analyzed for tetra- through octa- PCDD and PCDF including all individual 2,3,7,8-substituted isomers using HRGC with high-resolution mass spectrometry (HRMS) and a DB5 column.

A batch of Teflon filters were extracted by methylene chloride according to CARB 429 and the extract was analyzed for PAH and PCDD/PCDF species. No reagent blanks were analyzed.

For the PAH analyses, some of the internal recoveries were below the 50% recovery limit on the initial analytical runs. In all cases the internal instrument responses were well above a 10:1 signal to noise ratio and all recoveries were 33% or better for the sample runs, allowing isotope dilution for all analytes. To confirm the lower than optimal recoveries, however, the archive portions of the extracts were cleaned and re-analyzed for those samples possessing internal recoveries below 50%. These results showed improvement in recoveries on some samples but poorer recoveries on others. The re-analysis data from the archived portions of the extracts confirms the original analytical results from prior runs, and points to matrix interferences as the cause of low internal recoveries for PAH.

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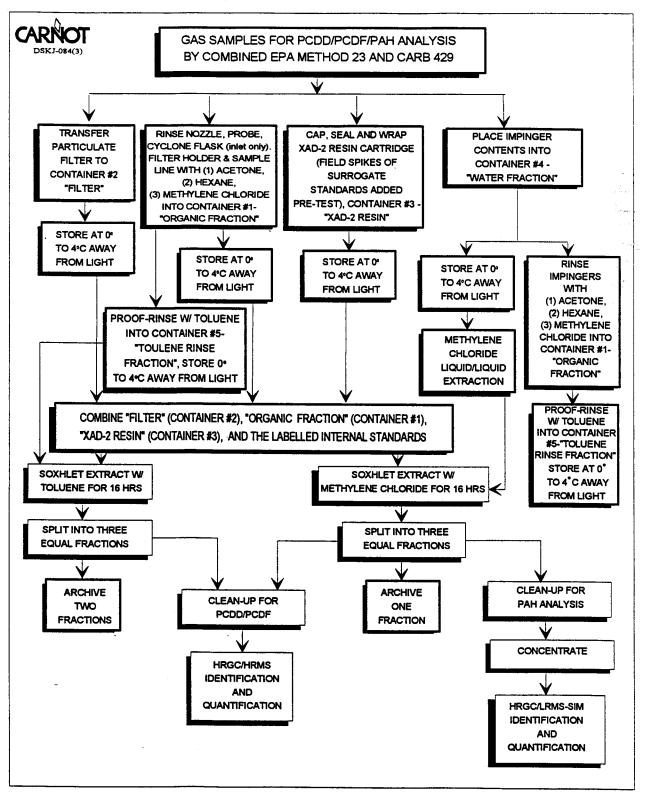


Figure 3-8. PCDD/PCDF/PAH Analysis

Approximately one-half of 3-SV-IN toluene fraction was inadvertently spilled in the laboratory and therefore analyzed separately from the other train fractions.

3.2.7 <u>VOST</u>

Benzene and toluene collected on the tenax and tenax/charcoal tube samples were prepared for analysis using EPA Method 5040, a purge and trap desorption GC/MS procedure. Condensate sample fractions are prepared according to EPA 5030. Analysis of the samples and condensates were performed by Zenon according to EPA 8260. The contents of the sorbent cartridges are spiked with internal and surrogate standards, thermally desorbed using helium gas, bubbled through reagent water, and captured on an analytical adsorbent trap. After desorption, the contents are heated and the volatile compounds are separated by high resolution gas chromatography and analyzed by low resolution mass spectrometry.

In general, the traps from the sample runs contained high, gram levels of condensed water. High moisture levels caused significant disruptions to the purge flow during trap desorption and therefore gave erratic and often low recoveries of internal and surrogate standards. Although the test plan called for analyzing only three of the four trap pairs, all four trap pairs from each sample run were analyzed and reported (when valid) to better estimate benzene and toluene source concentrations in light of these poor recoveries. Three trap pairs were desorbed and analyzed as one combined sample, and one pair was analyzed separately to assess breakthrough. Condensate fractions from each trap pair of a single sample run (four trap pairs) were combined for a single analysis. In addition to two field blanks per location, one trip blank and four lab blanks were also analyzed along with the samples.

3.2.8 Formaldehyde

The high pressure liquid chromatography (HPLC) analytical procedures for the quantification of formaldehyde were performed by Zenon as specified in EPA Method 0011A. Formaldehyde reacts with the aqueous acidic solution of 2,4-dinitrophenylhydrazine (DNPH) by nucleophilic addition to the carbonyl, followed by 1,2-elimination of water to form the 2,4-dinitrophenylhydrazone derivative. Acid is required to promote protonation of the carbonyl because DNPH is a weak nucleophile. Following train recovery, samples were chilled immediately in the field to stabilize the DNPH-carbonyl derivatives. Both DNPH and MeCl₂ rinses were used to recover the sample trains. These rinse fractions were combined in the laboratory for a single analysis.

Due to severe reagent and field blank formaldehyde contamination problems encountered on previous test programs using this method, Carnot added several extra quality assurance/quality

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control (QA/QC) steps to our sample handling protocol in an attempt to mitigate these contamination problems, namely:

- Cardboard boxes were replaced with a wooden crate for shipping the samples.
- Custom organic-free amber glass sample bottles were designed with a 750ml capacity that is large enough to contain a single sample.
- Sample bottles were pre-cleaned by Zenon. DNPH reagent supplied by Zenon for sampling and recovery was delivered on-site in these sample bottles.
- Each sample bottle was stored in air-tight Teflon screw-top containers that contained activated carbon.
- To ship the samples back to Zenon after the test program, the Teflon containers were purged and filled with nitrogen gas.

In addition to two field blanks (one per sample location), one reagent/trip blank was analyzed along with the samples.

3.2.9 Sulfur Oxides

Back-half sample train fractions are recovered with DI H₂O for sulfate analysis by Carnot using EPA Method 8. The quartz wool plug is added to the rinse of the condensate coil which is analyzed for sulfate and reported as SO₃. The sample line and peroxide impinger contents and rinse are recovered into a separate sample bottle, analyzed for sulfate, and reported as SO₂. Both samples are titrated by a barium chloride titration to determine their sulfate content. Isopropyl alcohol is added to the sample before it is titrated with barium chloride in the presence of a modified thorin green indicator. The end point of the titration is the formation of the ink-grey barium sulfate complex. A peroxide reagent blank was taken in the field and analyzed along with the samples.

3.2.10 Particle Size Distribution

Following the test, the seven impactor separation stages and back-up filter are quantitatively recovered, baked at 105°C, desiccated and weighed until a constant weight is found (less than 0.5mg difference between consecutive 6-hour weighings). The preseparator is rinsed with acetone, and the acetone is evaporated in a tared container for a gravimetric PM>10 micron determination. An acetone reagent blank was also analyzed. Carnot performed the particle size distribution analyses in-house.

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3.2.11 Solid Samples

Solid samples include the coal feed, bottom ash, flyash, limestone solids, and gypsum solids. As-received and residual moisture levels were determined from the gross sample sizes through a series of weighings, air drying, top size reductions, sample size reductions, and high-temperature baking. Fifty gram, -60 mesh sample splits were obtained according to ASTM D2013-72 and analyzed using the procedures outlined in Table 3-6. ASTM instrumental techniques were used for determining the carbon, hydrogen, nitrogen, sulfur, moisture and ash content of the solid samples.

Major ash elements including phosphorus were analyzed by ICP-AES after an open pressure HNO₃/HF/HCl digestion. Coal samples were ashed at 750°C as per ASTM D3682-78 prior to acid digestion for the major ash elements.

Solid samples for trace element analyses (except antimony in the coal) were microwave-assisted acid digested using EPA SW846-3051 modified for a closed pressure digestion procedure. Sulfuric and nitric acids were used to digest the coal, and HNO₃, HF, and HCl were used to digest the ash and FGD solids. EERC has specially developed this complicated solids digestion procedure that consists of several microwave heating, cooling, and venting steps to obtain clear, solubilized solutions. ICP-AES was used to analyze most elements; GFAA was used for antimony, arsenic, cadmium, and lead in the ash samples; CVAAS was used for mercury; and HGAAS was used for selenium determination.

The coal samples for antimony analyses were ashed at 500°C as per ASTM D3683-78, open pressure acid digested using HNO₃/HF/HCl, and analyzed by GFAA.

With the exception of fluorine in the coal, chlorine and fluorine levels were determined in the solid samples using ASTM D4208-83 and ASTM D3761-84, respectively, which call for a 1350°C oxygen bomb combustion of the samples followed by an ion-selective electrode analysis of a dilute base scrubber solution. Coal samples for fluorine determination were gradually introduced into a 1150°C tube furnace while humidified air was passed over the sample. The condensate from this pyrohydrolysis technique contains volatile fluoride species trapped in a weak-base scrubber solution, which is then analyzed by ion-selective electrode for fluorine.

3.2.12 Liquid/Sludge Samples

FGD and WWTP liquid/sludge samples were microwave-assisted acid digested according to EPA Methods SW846-3015/3051 procedures. Most major and trace elements were analyzed by ICP-AES (EPA SW846-6010). Arsenic, lead, and selenium were analyzed by GFAA (EPA

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SW846-7000 series), and antimony, cadmium, and beryllium were analyzed by both procedures depending on sample type. CVAA (EPA SW846-7470) was used for mercury determination on all samples. Chloride and sulfate were analyzed by ion-chromatography according to EPA 9057 following a water extraction of the sludge samples. Fluoride was determined using EPA Method 13B which calls for a distillation of the sample before ion-selective electrode analysis. Moisture levels were obtained on the sludge samples gravimetrically. At the request of EPRI for informational purposes, alkalinity, hardness, pH, TDS/TSS, nitrates, and nitrites were also determined from the PWRF outlet and WWTP liquid samples.

3.3 SAMPLE HANDLING AND PRESERVATION

Table 12 presents the sample handling and preservation strategy for the NYSEG Milliken Unit 2 test program. Laboratory grade acid-washed HDPE Nalgene® sample bottles were used for the majority of the samples. An on-site refrigerator was used to store the samples at ≈4°C. Zenon picked-up their inorganic and organic samples at the conclusion of the test program by ground transportation. Organic sample analyses began immediately upon their arrival at Zenon. Metals speciation samples were shipped-out from the site to RTI and Frontier Geosciences. The solid samples were stored in 5-gallon plastic buckets and picked-up after the test program was complete by CTE.

TREATMENT OF NON-DETECTS, REAGENT/FIELD BLANK VALUES AND UNCERTAINTY CALCULATIONS

This section describes how non-detect and reagent/field blank values were treated in presenting the results in this test report. A description of how the uncertainties were calculated concludes this section.

3.4.1 Non-Detects

The discussion presented below explains how averages, sums and reported emission values were calculated for all species given various combinations of detected and non-detected values.

All values detected. The arithmetic average or sum is taken, as appropriate. No special techniques required.

All values below the detection limit. For individual test runs or species, the data is reported as "ND < (detection limit)." For cases where all three runs are below the detection limit, the average is reported as "ND < (average detection limit)."

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TABLE 3-7 SAMPLE HANDLING PROCEDURES NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

Sample					
	Parameter	Sample Description	Sample Container	Sampling Handling and Preservation	Laboratory
lue Ga	s Samples:				
	Multi-Metals	1 filter, 1-500 ml nitric acid rinse front half, 1-500 ml acetone rinse front half, 1-1500 ml nitric acid rinse back half, 1-200 ml nitric acid rinse middle knockout, 1-500 ml permanganate rinse, 1-200 ml HCl rinse		Zenon picked-up samples immediately at the conclusion of the test program. Seal and mark liquid level.	Zenon Environmenta 5555 N. Service Roa Burlington, Ontario CANADA L7L 5H7
2)	Hexavalent Chromium	Filtered KOH from impingers and rinses of train	1000 ml acid-washed HDPE bottle	Check pH ≥8; Seal and mark liquid level. Ship overnight immediately at	RTI Research Triangle
3)	Frontier Geoscience	Probe w/quartz wool plug, KCI/soda lime cartridge, Charcoal cartridge	Recovered at lab Glass/teflon cartridge Glass/teflon cartridge	the conclusion of the test program. Seal Seal Seal, shipped overnight after test program complete.	Park, NC Frontier Geosciences 414 Pontius North Seattle, WA 98109
4)	Solid Particulate	Filter, front half acetone rinse	500 ml amber glass bottles with teflon lid	Seal and mark liquid levels, after gravimetric analyses resolubilize and use one-half for anion analysis, save remaining portion	Zenon Environmenta
	Anions	1-1500 ml rinse bicarb impingers, 1-500 ml rinse H ₂ O ₂ impingers	500/1000 ml HDPE bottle and lid	Seal and mark liquid levels, save one- half for confirmation	
5)	PCDD/PCDF/PAH	Filter, wrapped XAD-2 column, 2-500 ml organic rinses, 2-500 ml water rinses	Organic-free amber glass jars with teflon lined lids, teflon taped	Samples extracted within 7 days of sampling; analysis performed within 21 days; stored samples at ≤ 4°C; Zenon picked-up immediately at the conclusion of the test program.	Zenon Environmenta
6)	VOST	4 tenax and tenax charcoal tube pairs, 40 ml water condensate rinse	Organic-free glass vials with teflon lined caps, teflon taped	Stored at < 4°C; picked-up immediately after the organic test period. Analyzed within 14 days.	Zenon Environmenta
7)	Formaldehyde	1-750 ml DNPH impingers/ rinse	Organic-free 750 ml glass sample jar with teflon lined lid, teflon taped	Stored samples at < 4°C; picked-up immediately after organic test period. Analyzed within 14 days.	Zenon Environmenta
8)	Particle Size Distribution	9 filters	Petri dishes	Seal. Ship to Carnot.	Carnot Tustin, CA
9)	Sulfur Oxides	50 ml DI H ₂ O condenser coil rinse, quartz wool, 500 ml peroxide impingers	250 and 500 ml HDPE bottles and lids	Seal and mark liquid level. Ship to Carnot	Carnot Tustin, CA

Note: Ontario-Hydro and TRIS Buffer samples were analyzed on-site.

Some values are detected and some are non-detects. As an approximation, half of the detection limit will be used for non-detect values and the full value for detects. As an example of averaging, an average for three tests runs with results of 10, 8, and ND < 6 would be 7. As an example for summing (such as for anion fractions), individual species values of 5, 8, ND < 1, and ND < 2 would be summed to provide a value of 5+8+0.5+1, or 14.5. In reporting these

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types of sums or averages, no "<" sign is used. The only exception to this rule occurs when the average is less than the highest detection limit of the non-detected values. In this case, the average is reported as "ND < (the highest detection limit)." For example, 5, ND < 4 and ND < 3 would be reported as "ND < 4." For calculating APCD removal efficiencies when the inlet stream is reported above the detection limit but the outlet is below, a ">" sign is used with the percent removal value.

3.4.2 Reagent/Field Blank Values

In general, when reagent blank levels are found to contribute consistently to the field blank and sample values they are subtracted. Reagent blanks are considered representative of the batch of reagent used for testing. In no case were sample results blank corrected to levels below their analytical detection limit. When subtracting a reagent blank returned a value lower than the detection limit, the detection limit was used and reported as a "hit."

Field blanks are not subtracted from sample values when a single field blank is taken because it is considered only a qualitative assessment of the contamination level present in the samples. Only when more than one field blank are taken (ideally as many as there are samples) do they become a better means of quantitatively assessing the sample contamination level. For the Ontario-Hydro, TRIS Buffer and VOST tests, more than one field blank were taken and used for blank subtractions (as described below). Field blanks are intended to measure the amount of contamination introduced to the samples from a variety of sources that range from sample handling, sample train materials, sample recovery, and the reagents. It is assumed that by treating the field blanks as samples, their results will reflect actual sample contamination.

For each group of sample trains used on this test program, the following summarizes how many reagent and field blanks were taken in the field and what type of subtractions were made to the sample results:

EPA Method 29. Three reagent blanks, one for each inorganic test day, that include the test filter were analyzed along with the flue gas samples. Average detected reagent blank values were subtracted from sample results for both trace and major elements. One field blank for the ESP inlet/outlet location and one for the stack location collected prior to the inorganic test period, in addition to two more field blanks (same locations) collected at the end of the inorganic test period to compare with the "clean glass" field blanks, were also analyzed. The "clean glass" field blank collected at the ESP inlet/outlet was inadvertently lost during analysis.

Hexavalent Chromium. A single 0.1N KOH reagent blank was taken in the field, analyzed for Cr⁶⁺, and then subtracted from sample results based on calculated reagent volumes used. A 5N KOH reagent blank was inadvertently not taken, so the 0.1N KOH reagent blank

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level was used instead assuming the Cr⁶⁺ blank level did not originate from the ultra-pure laboratory grade KOH solids. The EPA Hexavalent Chromium Recirculation Method does not require a field blank to be taken.

Frontier Geoscience. An average value from two trip blanks were subtracted from detected sample results. No field blanks were taken.

Ontario-Hydro/TRIS Buffer. Daily field blanks taken at the ESP outlet/FGD inlet location for each method were subtracted from corresponding daily sample results from both locations. No reagent blanks were analyzed.

Particulate/Anions. No particulate was found in the acetone reagent blank so no subtractions were made. For anions, when chloride, fluoride, or sulfate were found in either the filter, acetone, bicarbonate, or peroxide reagent blanks, appropriate blank subtractions were made to detected sample values. A single particulate/anion field blank was taken at the ESP inlet/outlet and stack locations.

PCDD/PCDF/PAH. No reagent blanks were analyzed. One field blank was taken at the ESP inlet/outlet and stack locations, but no subtractions to sample results were made.

VOST. When appropriate a mean blank (average of two field blanks, one trip blank, and four lab blanks) was subtracted from sample values.

Formaldehyde. No formaldehyde was found in the DNPH reagent/trip blank. One field blank was taken at the ESP outlet and stack locations, but no subtractions to sample results were made.

Sulfur Oxides. A peroxide reagent blank was subtracted from sample results. No field blanks were taken.

Particle Sizing. No particulate was found in the acetone reagent blank. No field blank was taken.

Semtech Hg 2000 Analyzer. Detector and reference zero and span values were adjusted after setting-up the analyzer at the stack location. The analyzer was auto-zeroed and zero-checked on ambient air daily.



3.4.3 <u>Uncertainty Calculations</u>

A 95% confidence interval will be calculated for each average emissions value presented. The interval is expressed as a percentage of the mean. The confidence limits were calculated as follows:

Uncertainty @ 95%
$$CI$$
,% = $\frac{S_{\bar{x}} * t_{N-1}/\sqrt{N}}{\bar{x}} * 100$

where:

 \bar{x} = Average sample value three replicates;

 $S_{\bar{x}}$ = Sample standard deviation;

 t_{N-1} = Student "t" factor for a two-tailed distribution at 95% for N-1 degrees of

freedom (4.3 for N=3); and

N = Number of replicates or measurements.

Uncertainty calculations assume the population distribution of each measurement is normally distributed and that the samples collected reflect the true population.

SECTION 4.0

FLUE GAS TEST RESULTS

This section presents the results of the exhaust gas tests performed at the ESP inlet, ESP outlet/FGD inlet, and FGD outlet/stack locations. Not included in this section are the flue gas mercury speciation results (see Section 6.0) or comparisons between Unit 2 post-retrofit data and May 1994 Unit 2 baseline data (see Section 7.0). The section begins with a summary of the inorganic and organic test results, followed by a discussion on exhaust flow measurements and flue gas flows and conditions. Results tables and discussions are presented individually for each measurement method.

4.1 SUMMARY OF RESULTS

The results of the flue gas tests are summarized in the following tables:

- Table 4-1: ESP and FGD Removal Efficiencies for Inorganic Species
- Table 4-2: Summary of Detected Organic Species

4.2 EXHAUST FLOW MEASUREMENTS AND FLUE GAS CONDITIONS

Tables 4-3 and 4-4 provide a summary of flue gas flows and conditions for the inorganic and organic test periods. Each test location's exhaust gas O2, CO2, moisture, temperature, and flow rate levels were steady throughout the test period. The 0.5% O₂ drop in boiler O₂ between the inorganic and organic test periods resulted in an average drop of 0.4% O2 for the three sample locations, corresponding to a 2.5% drop in pitot flow rates. Average flue gas conditions for both test periods were:

O ₂ %		Flue Gas Tempe	erature	Exhaust Gas Flow Rate dscfm @ 68 °F:				
ESP Inlet	5.52	ESP Inlet	289	ESP Inlet	324,800			
ESP Outlet	4.83	ESP Outlet	287	ESP Outlet	326,300			
Stack	5.45	Stack	122	Stack	340,300			

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TABLE 4-1 ESP AND FGD REMOVAL EFFICIENCIES FOR INORGANIC SPECIES NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **AUGUST 1996**

Species Trace Metals		Flue Gas Emissio		ESP Removal	FGD Removal
	ESP INLET	ESP OUTLET	STACK	Efficiency	Efficiency
Trace Metals					
Antimony	23	0.19	ND< 0.08	99.17%	> 57.3%
Arsenic	489	1.73	0.91	99.65%	47.3%
Barium	4,869	2.1	1.2	99.96%	41.3%
Beryllium	52	0.03	0.02	99.94%	31.4%
Cadmium	3.5	ND< 0.04	0.05	> 98.77%	31.470
Chromium	689	0.20	0.15	99.97%	25.0%
Hexavalent Chromium	0.85	NP	0.63		25.9%
Cobalt	183	0.12	0.12	99.94%	23.770
Copper	475	0.90	0.69	99.81%	24.1%
Lead	309	0.56	0.63	99.82%	27.170
Manganese	1,373	0.61	1.9	99.96%	
Mercury	6.89	5.74	2.31	16.75%	 59.7%
Molybdenum	97	0.39	0.35	99.60%	9.4%
Nickel	528	0.15	0.33	99.97%	7.47a
Selenium ⁽¹⁾	26	35	21	NV	
Vanadium	1,129	1.1	0.69	99.90%	NV
	-,>	•••	0.09	99.90%	39.1%
Anion Precursors					
Chlorine					
Solid Fraction	2,362	ND< 3.1	ND< 3.3	> 99.87%	
Gaseous Fraction	62.828	65,157	396	- 77.8770	99.4%
Total	65,190	65.159	398	0.05%	99.4%
Fluorine			370	0.0376	77.470
Solid Fraction	969	69.4	5.3	92.84%	92.3%
Gaseous Fraction	5,592	6,423	80	72.0470	92.3% 98.8%
Total	6,561	6,492	85	1.05%	98.7%
Sulfur	.,-	-,.,-	03	1.0376	98.770
Solid Fraction	28,372	1,126	2,082	96.03%	
Gaseous Fraction	1.84E+06	1.72E+06	1.17E+05	6.52%	93.2%
Total	1.87E+06	1.73E+06	1.19E+05	7.88%	93.1%
			1.176.103	7.0070	93.1%
Particulate. Ib/10 ⁶ Btu	6.35	0.007	0.014	99.88%	
Major Elements	lb/10 ⁶ Btu	<u>lb/10¹²Btu</u>	<u>lb/10¹²Btu</u>		
Aluminum	0.675	155	61	99.98%	(0.(0)
Calcium	0.228	196	259		60.6%
Iron	0.821	85	27	99.91%	
Magnesium	0.037	15	104	99.99%	68.6%
Phosphorus '	0.017	66	15	99.96%	
Potassium	0.092	28	ND< 38	99.62%	76.5%
Sodium	0.038	108	ND< 38	99.97%	
Titanium	0.035	11	6.3	99.72%	
	0.033	11	د.ه	99.97%	44.7%

NP: measurement not performed

NV: not valid

Note: (1) From comparisons with coal feed and flyash levels, selenium results for the ESTITE ASSIFIED are severely biased low; subsequently ESP and FGD removal efficiencies are not valid for selenium.

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TABLE 4-2
SUMMARY OF DETECTED ORGANIC SPECIES
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

	Trace Orga	nic Measurements, lb	/10 ¹² Btu
Parameter	ESP Inlet	ESP Outlet	Stack
Polycyclic Aromatic Hye	drocarbons:		
Naphthalene	7.2	9.4	10
2-Methylnaphthalene	0.028	0.027	0.23
Acenaphthylene	ND< 0.002	0.003	ND< 0.006
Acenaphthene de la contraction del contraction de la contraction d	0.015	ND< 0.057	ND< 0.009
Phenanthrene	0.003	ND< 0.022	0.10
Anthracene	0.020	0.014	ND< 0.003
PCDD/PCDF Isomers:			
2378-TCDD	ND< 1.5E-06	1.8E-06	1.7E -0 6
12378 PeCDD	1.4E-06	1.2E-06	ND< 1.3E-06
123478 HxCDD	3.7E-06	3.4E-06	3.2E-06
1234678 HpCDD	2.1E-06	8.6E-07	ND< 2.1E-06
OCDD	9.0E-06	3.4E-06	6.5E - 06
2378 TCDF	ND< 1.9E-06	ND< 7.5E-07	2.2E-06
12378 PeCDF	8.5E-07	ND< 7.3E-07	ND< 5.8E-07
23478 PeCDF	ND< 1.0E-06	ND< 8.6E-07	1.0E-06
123789 HxCDF	2.9E-06	ND< 4.7E-06	3.1E-0
OCDF	1.9E-06	ND< 1.1E-06	2.4E-0
Volatile Organic Comp	ounds:		
Benzene	NP	6.7	3.4
Toluene	NP	56	19
Formaldehyde	NP	0.83	8.8

NP: not performed



TABLE 4-3
FLUE GAS FLOWS AND CONDITIONS -- INORGANIC TEST PERIOD
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

									4.13.1475	HEAT BATE	% DIFF.	ISOKIN-
		- -				FLUE		PITOT	UNIT	HEAT RATE		
							SAMPLE	FLOW	LOAD.	FLOW	Pitot	ETIC
			$O_{\underline{1}}^{(1)}$.	CO ₂ ⁽²⁾ .	H2O.	TEMP.,	OLUME	RATE,	NET	RATE.	VS.	RATIO,
TEST NO.	DATE	TIME	%	%	%	F	dscf	dscfm	MW	dscfm ⁽³⁾	Heat Rate	%
TEST NO.												
1-MTLS-IN	08/07/96	0817/1227	5.60	13.86	8.5	293	137.91	325,318	149	337,574	-3.6	99.0
I-MTLS-OUT	08/07/96	0833/1512	5.38	14.06	8.3	284	221.74	323,354	149	332,789	-2.8	107.5
1-MTLS-STK	08/07/96	0817/1441	5.66	13.81	14.4	119	241.79	358,667	149	338,903	+5.8	97.0
I-PM/AN-IN	08/07/96	1044/1249	5.66	13.84	9.2	294	69.01	319,669	149	338,903	-5.7	101.5
I-PM/AN-OUT	08/07/96	0927/1357	5.38	14.09	8.7	297	152.52	325,883	149	332,789	-2.1	107.7
I-PM/AN-STK	08/07/96	0818/1230	5.77	13.74	14.1	125	141.02	336,350	149	341,367	-1.5	100.3
I-MESA-OUT	08/07/96	1025/1325	5.20	14.25	NA	NA	2.41	SP	149	SP	••	NA
I-MESA-STK	08/07/96	1050/1350	5.63	13.86	NA	NA	1.80	SP	149	SP		NA
1-SO3-OUT	08/07/96	1543/1643	5.57	13.86	7.8	NA	48.29	SP	149	SP		NA
1-SO3-STK	08/07/96	1545/1730	5.52	13.91	14.5	127	35.33	333,778	149	335,818	-0 .6	100.2
I-PSD-OUT	08/07/96	1615/1715	5.68	13.76	8.2	301	29.35	SP	149	SP		92.6
1-130-001	00/07/70	1015.1.15	2.00									
2-MTLS-IN	08/08/96	0803/1212	5.10	13.94	8.7	292	144.70	340,247	150	329,765	+3.2	99.3
2-MTLS-OUT	08/08/96	0822/1435	5.10	13.94	8.4	286	219.80	331,647	150	329,765	+0.6	101.7
2-MTLS-STK	08/08/96	0811/1540	5.52	13.57	14.8	119	253.28	358,779	150	338,771	+5.9	101.6
2-PM/AN-IN	08/08/96	0844/1255	5.53	13.58	8.0	292	150.44	344,157	150	338,991	+1.5	102.8
2-PM/AN-OUT	08/08/96	0854/1258	5.61	13.51	8.4	296	162.93	336,795	150	340,765	-1.2	100.7
2-PM/AN-STK	08/08/96	0802/1215	5.51	13.60	14.4	128	142.43	334,520	150	338,550	-1.2	101.9
2-MESA-IN	08/08/96	0840/1040	6.13	12.93	NA	NA	1.64	SP	150	SP		NA
2-MESA-OUT	08/08/96	0845/1145	5.34	13.62	NA	NA	2.77	SP	150	SP		NA
2-MESA-STK	08/08/96	0845/1145	5.33	13.63	NA	NA	1.67	SP	150	SP	••	NA
2-SO3-OUT	08/08/96	1336/1436	5.48	13.59	9.0	NA	50.55	SP	150	SP		NA
2B-SO3-STK	08/08/96	1610/1730	5.40	13.42	16.6	124	36.90	329,113	150	336,148	-2.1	106.2
2-PSD-OUT	08/08/96	1415/1545	5.24	13.73	8.7	299	47.01	SP	150	SP		103.3
2-13D-001	00/00/70						6.4					
3-MTLS-IN	08/09/96	Q803/1210	5.79	13.64	8.5	289	135.15	327.659	149	344,476	-4.9	96.3
3-MTLS-OUT	08/09/96	0814/1435	5.04	14.32	8.1	280	216.78	330,081	149	328,186	+0.6	100.8
3-MTLS-STK	08/09/96	0815/1507	5.76	13.67	14.3	118	254.55	362,692	149	343,793	+5.5	101.0
3-PM/AN-IN	08/09/96	0915/1320	5.74	13.70	8.8	287	140.68	329,486	149	343,340	-4.0	100.4
3-PM/AN-OUT	08/09/96	0821/1254	4.98	14.38	8.4	290	147.65	341.319	149	326,949	+4.4	102.6
3-PM/AN-STK	08/09/96	0814/1230	5.76	13.68	15.5	123	143.22	331,279	149	343,793	-3.6	103.4
3-MESA-IN	08/09/96	0930/1140	5.40	13.64	NA	NA	1.71	SP	149	SP		NA
3-MESA-OUT	08/09/96	0845/1145	5.32	13.71	NA	NA	2.78	SP	149	SP		NA
3-MESA-STK	08/09/96	0827/1127	5.35	13.68	NA	NA	3.23	SP	149	SP	••	NA
3A-MESA-IN	08/09/96	1340/1540	5.23	13.75	NA	NA	1.97	SP	149	SP		NA
3A-MESA-OUT		1245/1545	5.33	13.66	NA	NA	2.76	SP	149	SP		NA
3A-MESA-STK		1215/1515	5.33	13.66	NA	NA	2.86	SP	149	SP		NA
3-SO3-OUT	08/09/96	1335/1435	5.77	13.58	7.7	NA	50.06	SP	149	SP		NA
3A-SO3-STK	08/09/96	1300/1420	5.73	13.62	14.3	123	36.76	334,012	149	343,113	-2.7	104.2
3B-SO3-STK	08/09/96	1505/1615	5.81	13.66	14.7	123	36.23	331,223	149	344,932	-4.0	103.6
3-PSD-OUT	08/09/96	1315/1445	5.50	13.86	8.5	289	48.85	SP	149	SP		104.5
3-F3D-00 I	00,07,70											Std. Dev.
ESP Inlet Aver			5.57	13.76	8.6	291		331,089		338,842	-2.3	3.7
ESP Outlet Aver	-		5.25	14.05	8.4	289		331,513		331,874	-0.1	2.6
Stack Average	-		5.64	13.67	14.8	123		341,041		340,519	+0.2	4.0
DIEFE VALUE												

NA -- not available

SP -- single port traverse

Notes:

BY WHA DATE 3-14-20

⁽¹⁾ Test O2 levels measured using daily calibrated portable Teledyne O2 meters (electrochemical cell).

⁽²⁾ Stack CO₂ levels taken from Unit 2 CEMS located at the FGD stack location for corresponding time periods.

ESP inlet and outlet CO₂ levels calculated for each test period using corresponding stack CO₂ levels corrected from stack O₂ values to oxygen levels found at that location.

⁽³⁾ Calculated Heat Rate Flow Rate, dscfm = Boiler Eff., 9745 Btu/kW-hr * Unit 2 Load, MW (gross) * 1000 * F-Factor, dscf/MMBtu / 10^6 *

^{20.9/(20.9-}Flue Gas, O2%) / 60 min/hr

TABLE 4-4
FLUE GAS FLOWS AND CONDITIONS – ORGANIC TEST PERIOD
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

						FLUE		PITOT	UNIT	HEAT RATE	% DIFF,	ISOKIN-
							SAMPLE	FLOW	LOAD.	FLOW	Pitot	ETIC
			O ₂ (1).	CO ₂ ⁽²⁾ .	H2O.		OLUME	RATE.	NET	RATE,	VS.	RATIO,
			•			F	dscf	dscfm	MW	dscfm ⁽³⁾	Heat Rate	%
TEST NO.	DATE	TIME	%	%	%		dsci	asciiii	141 44	daciiii	Tical Rate	
. CV IN	08/12/96	0851/1255	5.40	14.00	8.1	288	124.74	313,044	148	333,129	-6.0	95.1
I-SV-IN		0851/1256	4.40	14.90	7.8	279	136.69	321,952	148	312,939	+2.9	97.7
1-SV-OUT	08/12/96	0918/1327	5.45	13.95	14.3	119	149.50	343,069	148	334,207	+2.7	104.3
1-SV-STK	08/12/96 08/12/96	1246/1454	5.60	13.66	9.4	289	68.88	324,097	148	337,483	-4 .0	101.4
I-CR-IN	08/12/96	1240/1540	5.44	13.80	11.8	120	103.47	SP	148	SP		100.0
1-CR-STK	08/12/96	1707/1907	6.00	13.61	8.0	288	68.30	SP	148	SP	-	101.0
1-SE-IN	08/12/96	1705/1905	4.95	14.57	8.1	291	65.20	SP	148	SP	_	102.5
1-SE-OUT	08/12/96	1450/1510	4.50	14.78	NA	NA	0.686	SP	148	SP		NA
IA-VOST-OUT	08/12/96	1450/1510	5.70	13.70	NA	NA	0.647	SP	148	SP		NA
IA-VOST-STK	08/12/96	1525/1545	4.50	14.78	NA	NA	0.673	SP	148	SP	-	NA
IB-VOST-OUT	08/12/96	1525/1545	5.70	13.70	NA	NA	0.658	SP	148	SP	-	NA
IB-VOST-STK	08/12/96	1559/1619	4.50	14.93	NA	NA	0.703	SP	148	SP		NA
1C-VOST-OUT	08/12/96	1559/1619	5.80	13.75	NA	NA	0.660	SP	148	SP		NA
IC-VOST-STK	08/12/96	1630/1650	4.70	14.81	NA	NA	0.670	SP	148	SP		NA
ID-VOST-OUT		1630/1650	5.80	13.80	NA	NA	0.640	SP	148	SP		NA
ID-VOST-STK	08/12/96	1630/1030	3.60	13.00		,						
2-SV-IN	08/12/96	1540/1944	5.73	13.81	7.8	287	131.80	319,429	147	340,505	-6.2	98.4
2-SV-IN 2-SV-OUT	08/12/96	1443/1852	4.96	14.51	7.7	283	138.35	320,301	147	324,056	-1.2	99.4
	08/12/96	1510/1920	5.78	13.76	14.6	118	144.29	341,987	147	341,631	+0.1	100.9
2-SV-STK	08/12/96	1709/1729	4.60	14.85	NA	NA	0.668	SP	147	SP	_	NA
2A-VOST-OUT	08/12/96	1709/1729	5.70	13.85	NA	NA	0.664	SP	147	SP	-	NA
2A-VOST-STK		1739/1759	4.70	14.81	NA	NA	0.664	SP	147	SP		NA
2B-VOST-OUT	08/12/96	1739/1759	5.70	13.90	NA.	NA	0.669	SP	147	SP	-	NA
2B-VOST-STK	08/12/96	1808/1828	4.70	14.81	NA	NA	0.694	SP	147	SP		NA
2C-VOST-OUT	08/12/96	1808/1828	5.80	13.80	NA	NA	0.671	SP	147	SP		NA
2C-VOST-STK	08/12/96	1842/1902	4.70	14.41	NA	NA	0.679	SP	147	SP		NA
2D-VOST-OUT	08/12/96	1842/1902	5.50	13.70	NA	NA	0.667	SP	147	SP	_	NA
2D-VOST-STK	08/12/96	1842/1702	3.50	13.70								
2 CV D	08/13/96	0820/1225	5.15	14.17	7.9	283	127.23	311,472	149	322,121	-3.3	97.5
3-SV-IN	08/13/96	0832/1240	4.22	15.00	8.2	278	136:90	321,047	149	304,161	+5.6	98.2
3-SV-OUT	08/13/96	0835/1245	4.98	14.32	14.3	118	144.92	328,348	149	318,681	+3.0	105.6
3-SV-STK	08/13/96	0954/1244	5.32	14.21	8.8	288	69.44	318,111	149	325,635	-2.3	104.2
2-CR-IN	08/13/96	0830/1130	5.24	14.28	13.5	121	107.17	SP	149	SP	-	101.3
2-CR-STK	08/13/96	1449/1701	5.64	13.84	8.5	290	70.59	325,275	149	332,464	-2.2	103.5
3-CR-IN	08/13/96	1445/1745	5.33	14.12	14.6	122	106.56	SP	149	SP	-	101.9
3-CR-STK	08/13/96	1200/1402	4.44	14.57	8.0	295	66.41	316,771	149	308,226	+2.8	99.3
1-FORM-OUT	08/13/96	1215/1420	4.66	14.38	14.5	123	68.25	320,789	149	312,401	+2.7	101.8
1-FORM-STK	08/13/96	1401/1606	3.97	15.22	8.0	282	71.16	319,404	149	299,66 9	+6.6	105.5
2-FORM-OUT	08/13/96	1345/1550	5.12	14.19	14.4	120	73.93	348,971	149	321,508	+8.5	99.3
2-FORM-STK	08/13/96	1601/1816	4.49	14.80	8.6	295	72.49	326,628	149	309,165	+5.6	103.3
3-FORM-OUT		1605/1810	5.25	14.11	14.1	119	74.29	353,892	149	324,179	+9.2	100.5
3-FORM-STK	08/13/96	1144/1204	4.70	14.77	NA	NA	0.679	SP	149	SP		NA
3A-VOST-OUT		1144/1204	5.00	14.50	NA	NA	0.622	SP	149	SP	-	NA
3A-VOST-STK		1212/1232	4.70	15.06	NA		0.681	SP	149	SP		NA
3B-VOST-OUT		1212/1232	5.30	14.50	NA		0.638	SP	149	SP	_	NA
3B-VOST-STK		1212/1252	4.70	14.57	NA		0.682	SP	149	SP	-	NA
3C-VOST-OUT		1242/1302	5.00	14.30	NA		0.660	SP	149	SP		NA
3C-VOST-STK		1322/1342	4.80	14.74	NA		0.683	SP	149	SP		NA
3D-VOST-OUT		1357/1417	5.80	14.74	NA		0.648	SP	149	SP		NA
3E-VOST-STK	08/13/96	133//191/	3.60	17.20	11/1							Std. Dev.
202 T 1			5.47	13.95	8.4	287		318,571		331,889	-4.0	1.8
ESP Iniet Aver	-		4.41	14.83	8.1			321,017		309,703	+3.7	2.9
ESP Outlet Av	-		5.25		14.0			339,509		325,434	+4.4	3.6
Stack Average	ş:		<i>د</i> ے۔ د	17.10							-	

NA - not available

SP - single port traverse

Notes: (See "Notes" from Table 4-3)



The average oxygen levels measured at the ESP inlet are 14% higher than those measured at the ESP outlet. It is unlikely that the oxygen level actually decreased across the ESP, suggesting that a leak in the ESP inlet sampling trains and/or measurement error has introduced additional uncertainty in these oxygen measurements and subsequent emission factor calculations.

As a quality assurance check on the pitot measurements of the exhaust gas flow rates, they were calculated stoichiometrically from an EPA Method 19 F-factor, a Unit 2 boiler efficiency factor of 9745 Btu/kW-hr, and Unit 2 gross megawatts. These calculated values, given in Tables 4-3 and 4-4, show excellent agreement with measured flow rates with differences ranging from 0.1-4.4%.

4.3 TRACE AND MAJOR ELEMENTS

ESP removal efficiencies presented on Table 4-1 averaged 99.73% for trace metals excluding mercury and selenium, and 99.89% for major elements, compared to a total particulate removal efficiency of 99.88%. These results show consistent ash removal and serve as a positive quality assurance indicator. When reportable, FGD removal efficiencies for trace metals averaged 36.0% and for major elements 62.6%. Mercury removal across the ESP averaged 17% and across the FGD it increased to 60%. An increase in concentration levels across the FGD can be seen for cadmium, cobalt, lead, manganese, nickel, calcium, and magnesium. This increase is considered significant only for manganese and magnesium since these elements exist at levels in the limestone that exceed gypsum concentrations. For the remaining elements, differences between ESP outlet and stack concentration levels are within the method's uncertainty range.

Severe negative matrix interferences from the high levels of sulfur found in the ESP inlet and ESP outlet samples tremendously hindered their analyses for selenium. As much as possible, the sample preparation and analytical techniques were optimized for selenium to overcome these matrix interferences. Zenon initially attempted to analyze these samples for selenium using GFAA and ICP-MS, but matrix spike recoveries were too low to consider these analytical results valid. More acceptable matrix spike recoveries were obtained using HGAA; however, the reported levels of selenium were still low, and therefore questionable.

Given that the EPA Method 29 results from the May 1994 baseline test program also possessed severe low biases for selenium, Carnot/Zenon attempted to investigate the possibility that the nitric acid/peroxide impinger solution does not completely capture all the selenium present in the flue gas. A stronger oxidizing solution, similar to the acidified potassium permanganate solution used for mercury, could be necessary to collect all gaseous selenium species. To investigate this possibility, Zenon attempted to analyze the permanganate fraction for selenium. Again, sulfur interferences from the sulfuric acid used to acidify the permanganate

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resulted in questionable results. It is now believed that sulfur interferences are the main source for the low biases associated with the selenium analytical results for Milliken Unit 2. This would explain why the post-retrofit ESP inlet/outlet and May 1994 baseline selenium data are biased low, and at the same time why no significant matrix interferences were encountered during the analyses of the post-retrofit FGD outlet/stack samples.

From comparisons with coal input and flyash levels, the severe magnitude of the low bias associated with the ESP inlet/outlet selenium results is clear. Based on the selenium coal input of 88 lb/10¹²Btu and the flyash output of 19 lb/10¹²Btu, ESP inlet selenium levels should be in the 80-90 lb/10¹²Btu range as opposed to 26 lb/10¹²Btu, and the ESP outlet selenium results should be on the order of 60-70 lb/10¹²Btu well above the reported 35 lb/10¹²Btu. Coal selenium levels are considered valid for two reasons:

- 1) They agree with Consol's database for the type of coal fired during this test program.
- 2) Most of the sulfur present in the coal will be vaporized during digestion, and therefore will not be present in the digestate used for analysis.

Flyash selenium concentrations are considered valid also for two reasons:

- 1) Both Zenon and EERC analyzed different flyash sample groups using different digestion and analytical techniques, but produced similar results.
- 2) Very little sulfur (<0.5%) is present in the flyash.

Given the low levels of sulfur contained in the stack EPA Method 29 samples and the lack of matrix interferences encountered during analysis, the stack selenium results are considered valid. FGD mass balance results will not support the currently reported stack selenium level if the ESP outlet results are actually around 60-70 lb/10¹²Btu. It is believed, however, that the gypsum selenium results are also severely biased low due to the large amounts of sulfur (about 18%) present in these samples. This would resolve the FGD balance for selenium given the expected ESP outlet selenium concentration range of 60-70 lb/10¹²Btu.

Table 4-5 summarizes the EPA Method 29 test results for both the samples and field blanks. As indicated on the table, both sets of results were reagent blank corrected. Field blank levels for the ESP inlet and for major elements at all three test locations were not significant (less than 1/3 of sample result). ESP outlet field blank levels were significant for antimony, chromium, cobalt, copper, lead, manganese, and nickel. Average stack field blank levels were significant for chromium, copper, lead, molybdenum, and nickel. Only for chromium was there a notable increase between pre- and post-test stack field blank values. Overall, it is not surprising to see similar levels of trace metals in the samples and field blanks for the ESP outlet and stack considering how low the flue gas concentration levels are reported.

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TABLE 4-5
SUMMARY OF EPA METHOD 29 TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Element	Inorganic l	Flue Gas Emissi	ons, ug/Nm ³		Field Blank L	evels ug/Nm³	1)
	ESP INLET	ESP OUTLET	STACK	ESP INLET	ESP OUTLET	STACK	STACK
						(Pre-Test)	(Post-Test)
Trace Elements							*
Antimony	30	0.25	ND< 0.11	0.30	0.19	ND< 0.10	ND< 0.10
Arsenic	643	2.3	1.2	ND< 0.18	ND< 0.12	ND< 0.10	ND< 0.10
Barium ⁽²⁾	6,408	2.8	1.6	0.20	0.13	0.08	0.14
Beryllium	69	0.04	0.03	ND< 0.02	ND< 0.01	ND< 0.01	ND< 0.009
Cadmium ⁽²⁾	4.6	ND< 0.06	0.07	0.01	0.01	0.04	
Chromium ⁽²⁾	906	0.27	0.20	1.3	0.85	0.04	0.005
Cobalt	241	0.16	0.16	0.16	0.10	0.18 ND< 0.10	0.55
Copper	625	1.2	0.90	1.1	0.67	0.58	ND< 0.50
Lead ⁽²⁾	406	0.75	0.83	0.49	0.07		0.47
Manganese ⁽²⁾	1,808	0.82	2.5	0.49		1.4	0.05
Mercury	9.09	7.72	3.02	ND< 0.09	0.31	0.58	0.27
Molybdenum ⁽²⁾	128	0.52	0.46	0.27	ND< 0.06	0.05	0.03
Nickel ⁽²⁾	695	0.20	0.43		0.17	0.45	0.45
Selenium	35	47	27	0.38 ND< 0.19	0.24	0.41	ND< 1.0
Vanadium	1,486	1.5	0.89	ND< 0.19 ND< 0.46	ND< 0.12	ND< 0.11	ND< 0.11
	.,	1.5	0.69	ND< 0.46	ND< 0.29	ND< 0.26	ND< 0.26
ajor Elements, mg	/Nm³						
Aluminum ⁽²⁾	888	0.21	0.080	0.016	0.010	0.000	0.005
Calcium ⁽²⁾	300	0.26	0.34	0.11		0.006	0.006
Iron ⁽²⁾	1,081	0.11	0.035		0.068	0.15	0.04
Magnesium ⁽²⁾	49	0.020	0.033	0.001	0.001	0.003	0.0005
Phosphorus ⁽²⁾	22			0.00	0.003	0.010	0.002
Potassium	121	0.088	0.020	0.005	0.003	0.003	0.003
Sodium ⁽²⁾	50		ND< 0.050	ND< 0.04	ND< 0.026	ND< 0.050	ND< 0.050
Titanium	30 45	0.15	0.18	0.079	0.050	0.005	0.027
	43	0.015	0.008	ND< 0.002	ND< 0.001	ND< 0.001	ND< 0.001
Sulfur ⁽²⁾	2,467	2,320	155	0.051	0.032	0.029	NP

NP: measurement not performed

Notes:

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⁽¹⁾ Field blank levels calculated using the average sample volume from the metals tests at the corresponding sample location and subtracting the reagent blank level when appropriate.

⁽²⁾ Reagent blank subtractions were made from sample values (see results tables).

The following two sections discuss the trace and major element results for the flue gas streams. For the purposes of discussion, uncertainties @ the 95% confidence interval reported below 50% for the ESP inlet samples and below 100% for the ESP outlet and stack samples (due to lower concentrations) are considered acceptable. Higher uncertainties will be addressed.

4.3.1 Trace Metals

Table 4-6 presents the ESP inlet trace metal test results. Consistent with coal input levels, barium, manganese, and vanadium were the predominant elements measured. Separate analyses of the front-half solids revealed that 98-99% of reported trace metals (excluding mercury and selenium) were captured in the front-half of the sample train. 10.4% of total ESP inlet mercury was measured in the solids catch. The concentration of selenium found in the front-half solids agreed with flyash concentration levels, and amounted to 46% of the reported selenium value of 35 ug/Nm³. This leaves the back-half portion of the selenium sample train as the source for any biases in the results.

Table 4-7 presents the ESP outlet trace metal test results. Only cadmium was reported below the analytical detection limit. Significant (greater than 50%) reagent blank corrections were made for chromium, molybdenum, and nickel. Blank corrections did not exceed EPA Method 29 limits.

Stack trace metal results are given on Table 4-8. Only antimony was reported below the analytical detection limit. Poor agreement can be seen between lead and nickel replicates. It is clear from Table 4-5 and the pre-test versus post-test stack field blanks, that higher stack emissions for one lead and one nickel replicate were due to contamination associated with unclean glassware that became free of contamination as it was used for testing. Significant reagent blank corrections were made to chromium, molybdenum, and nickel results, but they did not exceed Method 29 limits.

4.3.2 Major Elements

Tables 4-9, 4-10 and 4-11 present the major element test results for the ESP inlet, outlet and stack, respectively. Concentration units are in mg/Nm³, ESP inlet emission factors are in lb/10⁶Btu, and ESP outlet and stack emission factors are in lb/10¹²Btu. Silicon was not available from the EPA Method 29 trains since a quartz-fiber filter is used for sampling. Total sulfur was measured on these samples to replace the invalid sulfur results from the particulate/anion trains. Sulfur, iron and aluminum were the predominant elements measured at the ESP inlet consistent with coal input levels. Significant blank corrections were made for iron and sodium for the ESP outlet and stack samples. Higher uncertainties for these elements is most likely due to inconsistent sources of contamination.

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TABLE 4-6
EPA METHOD 29 TRACE ELEMENT TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP INLET
AUGUST 1996

Test No. Date	1-MTLS-IN 8/7/96			N	AVERA	GE	Un	certainty	Avg. Blank
Pitot Flow Rate, dscfi		8/8/96	8/9/96				- @	95%CI	Correction,
Sample Volume, dscf	137.91	340,247 144.70	327,659						% of Sample
Fuel Factor, dscf/106H		12,739	135.15						Value
O ₂ , %	5.60	5.10	13,355 5.79						
CO ₂ , %	13.86	13.94	13.64						
H ₂ O, %	8.5	8.7	8.5						
Element u	g/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu	%		
A						io/10 Dta	/0	ug/Nm ³	
Antimony	31	26	32	30	0.034	23	26%	8	
Arsenic	713	602	615	643	0.74	489	23%	151	
Barium	6,913	6,026	6,286	6,408	7.39	4,869	18%	1132	0.020/
Beryllium	73	67	67	69	0.080	52	14%	9	0.02%
Cadmium	5.3	3.9	4.6	4.6	0.0053	3.5	37%	2	0.400/
Chromium	933	845	941	906	1.0	689	15%	133	0.48%
Cobalt	247	232	244	241	0.28	183	8%	20	0.15%
Copper	635	606	634	625	0.72	475	7%	41	
Lead	420	365	433	406	0.47	309	22%	90	
Manganese	1,782	1,817	1.824	1,808	2.1	1,373	3%		0.04%
Mercury	9.1	9.9	8.3	9.1	0.011	6.9		55	0.06%
Molybdenum	125	123	136	128	0.15	97	21%	2	
Nickel	715	675	696	695	0.80	528	13%	17	2.7%
Selenium	32 '		39	35	0.040	26	7%	50	0.27%
/anadium	1,553 _	1,403	1,502	1,486	1.7	1,129	29% 13%	10 190	

ND< - species not detected

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TABLE 4-7 EPA METHOD 29 TRACE ELEMENT TEST RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP OUTLET AUGUST 1996

Test No.	1-MTLS	-OUT 2-MTLS	S-OUT 3-MTL	S-OUT	AVERAC	E	I I		4 5: :
Date	8/7/96	8/8/96	8/9/96		AVEIGN	JL	_	ertainty	Avg. Blank
Pitot Flow Rate, dscfr	n 323,354	331,647	330,081				<u> </u>	95%CI	Correction,
Sample Volume, dscf	221.74	219.80	216.78						% of Sampl
Fuel Factor, dscf/106E	Stu 12.919	12,739	12,724						Value
O ₂ , %	5.38	5.10	5.04						
CO ₂ , %	14.06	13.94	14.32						
H ₂ O, %	8.3	8.4	8.1						
Element t	ıg/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu	%	ug/Nm³	
Antimony	0.27	0.24	0.24	0.25	2.9E-04	0.10			
Arsenic	3.0	2.6	2.3	2.3	2.9E-04 0.0027	0.19	17%	0.04	
Barium	2.5	2.7	3.1	2.3		1.7	34%	0.80	
Beryllium	0.04	0.04	0.05	0.04	0.0032 4.9E-05	2.1	26%	0.74	24%
Cadmium	0.06	ND< 0.06	ND< 0.06	ND< 0.06	ND< 6.6E-05	0.03	13%	0.01	
Chromium	0.38	0.21	0.23	0.27		ND< 0.04			6.0%
Cobalt	0.15	0.15	0.17	0.16	3.1E-04	0.20	85%	0.23	74%
Copper	1.4	1.2	1.0	1.2	1.8E-04	0.12	11%	0.02	
ead	0.60 '	0.95	0.72	0.75	0.0014	0.90	42%	0.5	
/langanese	1.0	0.73	0.72	0.73	8.7E-04	0.56	59%	0.44	12%
Mercury	6.9	8.9	7.4		9.3E-04	0.61	62%	0.50	46%
/lolybdenum	0.51	0.52	0.52	7.7	0.0089	5.7	33%	2.5	
lickel	0.28	0.19	0.32	0.52	5.9E-04	0.39	3%	0.01	75%
elenium	46	49	0.12 46	0.20	2.3E-04	0.15	100%	0.20	86%
anadium	1.4			47	0.054	35	9%	4	
	1.7	1.6	1.6	1.5	0.0017	1 1	220/	Λ2	

1.5

0.0017

1.1

22%

0.3

1.6

ND< - species not detected

TABLE 4-8
EPA METHOD 29 TRACE ELEMENT TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- STACK
AUGUST 1996

Date 8/7/96 8/8/96 8/9/96 8/9/96 9/9												1-4
Pitot Flow Rate, dscfm 358,667 358,779 362,692 362,692 358,667 358,779 362,692	Test No.	1-MTL	S-STK	2-MTLS-STI	C 3-MTLS	-STK		AVEDAC	CE.			
Pitot Flow Rate, dscfm 358,667 358,779 362,692 Sample Volume, dscf 241.79 253.28 254.55 Fuel Factor, dscf/10 ⁶ Btu 13,157 13,087 13,329 O ₂ , % 5.66 5.52 5.76 CO ₂ , % 13.81 13.57 13.67 H ₂ O, % 14.4 14.8 14.3 Element ug/Nm ³ ug/Nm ³ ug/Nm ³ ug/Nm ³ ug/Nm ³ lb/hr lb/10 ¹² Btu % ug/Nm ³ Antimony ND< 0.11 ND< 0.10 0.15 ND< 0.11 ND< 1.3E-04 ND< 0.08	Date							AVERA	JE	-	,	-
Sample Volume, dscf 241.79 253.28 254.55 Fuel Factor, dscf/10 ⁶ Btu 13.157 13.087 13.329 O ₂ , % 5.66 5.52 5.76 CO ₂ , % 13.81 13.57 13.67 H ₂ O, % 14.4 14.8 14.3 Element ug/Nm ³ ug/Nm ³ ug/Nm ³ ug/Nm ³ lb/hr lb/10 ¹² Btu % ug/Nm ³ Antimony ND< 0.11 ND< 0.10 0.15 ND< 0.11 ND< 1.3E-04 ND< 0.08	Pitot Flow Rate, dscf	m 358,667	,	358,779						(<u>a</u>)	95%CI	_
Value Fuel Factor, dscf/10 ⁶ Btu 13,157 13,087 13,329 O ₂ , % 5.66 5.52 5.76 CO ₂ , % 13.81 13.57 13.67 H ₂ O, % 14.4 14.8 14.3 Element ug/Nm ³ ug/Nm ³ ug/Nm ³ ug/Nm ³ lb/hr lb/10 ¹² Btu % ug/Nm ³ Antimony ND< 0.11 ND< 0.10 0.15 ND< 0.11 ND< 1.3E-04 ND< 0.08	Sample Volume, dscf	241.79			, -							-
O2, % 5.66 5.52 5.76 CO2, % 13.81 13.57 13.67 H2O, % 14.4 14.8 14.3 Element ug/Nm³ ug/Nm³ ug/Nm³ lb/hr lb/hr lb/10¹²Btu % ug/Nm³ Antimony ND< 0.11	Fuel Factor, dscf/10 ⁶ 1	Btu 13,157										Value
CO ₂ , % 13.81 13.57 13.67 H ₂ O, % 14.4 14.8 14.3 Element ug/Nm ³ ug/Nm ³ ug/Nm ³ ug/Nm ³ lb/hr lb/10 ¹² Btu % ug/Nm ³ Antimony ND< 0.11 ND< 0.10 0.15 ND< 0.11 ND< 1.3E-04 ND< 0.08	O ₂ , %	5.66		•								
H ₂ O, % 14.4 14.8 14.3 Element ug/Nm³ ug/Nm³ ug/Nm³ ug/Nm³ lb/hr lb/10 ¹² Btu % ug/Nm³ Antimony ND< 0.11 ND< 0.10 0.15 ND< 0.11 ND< 1.3E-04 ND< 0.08	CO ₂ , %	13.81										
Antimony ND< 0.11 ND< 0.10 0.15 ND< 0.11 ND< 1.3E-04 ND< 0.08	H ₂ O, %	14.4										
Antimony ND< 0.11 ND< 0.10 0.15 ND< 0.11 ND< 1.3E-04 ND< 0.08	Element	ug/Nm³	ug	g/Nm³ u	ıg/Nm³	ug/N	vm ³	lb/hr	lb/10 ¹² Btu	%	ug/Nm³	
Arsenic 1.2 1.0 1.0 1.2 0.0015 0.91 22% 0.26 Barium 1.4 1.6 1.8 1.6 0.0020 1.2 30% 0.47 33% Cadmium 0.03 0.03 0.03 0.03 3.6E-05 0.02 34% 0.01 Cadmium 0.07 0.05 0.09 0.07 8.8E-05 0.05 61% 0.04 15% Chromium 0.19 0.22 0.18 0.20 2.5E-04 0.15 30% 0.06 75%	Antimony NI	D< 0.11	ND<	0.10	0.15	NID -	0.11	ND < 1.25.04			ug/iviii	
Barium 1.4 1.6 1.8 1.6 0.0020 1.2 30% 0.47 33% Beryllium 0.03 0.03 0.03 0.03 3.6E-05 0.02 34% 0.01 Cadmium 0.07 0.05 0.09 0.07 8.8E-05 0.05 61% 0.04 15% Chromium 0.19 0.22 0.18 0.20 2.5E-04 0.15 30% 0.06 75%	Arsenic											
Beryllium 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.047 33% Cadmium 0.07 0.05 0.09 0.07 8.8E-05 0.05 61% 0.04 15% Chromium 0.19 0.22 0.18 0.20 2.5E-04 0.15 30% 0.06 75%	Barium	1.4										
Cadmium 0.07 0.05 0.09 0.07 8.8E-05 0.02 34% 0.01 Chromium 0.19 0.22 0.18 0.20 2.5E-04 0.15 30% 0.06 75%	Beryllium	0.03									0.47	33%
Chromium 0.19 0.22 0.18 0.20 2.5E-04 0.15 30% 0.06 75%	Cadmium										0.01	
0.10 0.20 2.5E-04 0.15 30% 0.06 750/	Chromium									61%	0.04	15%
.00ait 0.12 0.22 0.15 0.16 2.05.04	Cobalt	0.12		0.22					0.15	30%	0.06	75%

Antimony	ND< 0.11	ND< 0.10	0.15	ND< 0.11	ND< 1.3E-04	ND< 0.08			
Arsenic	1.2	1.0	1.0	1.2	0.0015				
Barium	1.4	1.6	1.8	1.6		0.91	22%	0.26	
Beryllium	0.03	0.03	0.03		0.0020	1.2	30%	0.47	33%
Cadmium	0.07			0.03	3.6E-05	0.02	34%	0.01	
Chromium		0.05	0.09	0.07	8.8E-05	0.05	61%	0.04	15%
	0.19	0.22	0.18	0.20	2.5E-04	0.15	30%	0.06	75%
Cobait	0.12	0.22	0.15	0.16	2.0E-04	0.12	85%	0.14	
Copper	1.0	0.91	0.79	0.90	0.0011	0.69			
Lead	1.6	0.61	0.31	0.83			28%	0.25	
Manganese	2.1	2.1	3.3		0.0010	0.63	194%	1.6	14%
Mercury	2.7	3.3		2.5	0.0031	1.9	70%	1.7	20%
Molybdenum		=	3.1	3.0	0.0038	2.3	21%	0.65	
Nickel	0.47	0.45	0.45	0.46	5.7E-04	0.35	7%	0.03	79%
	0.05	1.2	0.04	0.43	5.4E-04	0.33	385%	1.7	79%
Selenium	24	25	33	27	0.034	21	44%		19%
Vanadium	0.81	1.0	0.9	0.89				12	
			0.7	0.89	0.0011	0.69	20%	0.18	

ND< - species not detected

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NYS1A-11476/R107G404.T Rev. (June 6, 1997)

TABLE 4-9
EPA METHOD 29 MAJOR ELEMENT TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP INLET
AUGUST 1996

Test No.	I-MTLS-IN	2-MTLS-IN	3-MTLS-I	N	AVERA(GE	Unc	ertainty	Avg. Blank
Date	8/7/96	8/8/96	8/9/96				@9	95%CI	Correction,
Pitot Flow Rate, dscfm	325,318	340,247	327,659						% of Sample
Sample Volume, dscf	137.91	144.70	135.15						Value .
Fuel Factor, dscf/10 ⁶ B	tu 13,105	12,739	13,355						
O ₂ , %	5.60	5.10	5.79						
CO ₂ , %	13.86	13.94	13.64						
H ₂ O, %	8.5	8.7	8.5						
Element m	g/Nm³	mg/Nm³	mg/Nm³	mg/Nm³	lb/hr	lb/10 ⁶ Btu	%	mg/Nm	3
Aluminum	911	837	916	888	1,024	0.675	12%	109	0.005%
Calcium	281 '	313	306	300	347	0.228	14%	42	0.013%
Iron	1,100	1,063	1,079	1,081	1,248	0.821	4%	46	0.012%
Magnesium	45	53	50	49	57	0.037	19%	9	0.015%
Phosphorus Phosphorus	22	20	25	22	26	0.017	28%	6	0.089%
Potassium	118	116	128	121	139	0.092	14%	17	

- moobiio.es		20	22		20	0.017	20/0	U	0.007/0
Potassium	118	116	128	121	139	0.092	14%	17	
Sodium	54	47	49	50	58	0.038	17%	9	0.38%
Titanium	46	44	46	45	52	0.035	9%	4	
Sulfur	2,443	2,528	2,428	2,467	2,849	1.87	5%	134	0.004%

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TABLE 4-10
EPA METHOD 29 MAJOR ELEMENT TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP OUTLET
AUGUST 1996

Test No. Date Pitot Flow Rate, dscfn	1-MTLS-O1 8/7/96 n 323,354	U 2-MTLS-0 8/8/96 331,647	OUT 3-MTLS 8/9/96 330,081	-OUT	AVERA	GE		certainty 95%CI	Avg. Blank Correction,
Sample Volume, dscf Fuel Factor, dscf/10 ⁶ B O ₂ , % CO ₂ , % H ₂ O, %	221.74 tu 12,919 5.38 14.06 8.3	219.80 12,739 5.10 13.94 8.4	216.78 12,724 5.04 14.32 8.1		·				_% of Sampi Value.∴
Element m	g/Nm³	mg/Nm³	mg/Nm³	mg/Nm³	lb/hr	lb/10 ¹² Btu	%	mg/Nm ³	
Aluminum Calcium (ron Magnesium Phosphorus Potassium Godium Titanium	0.19 0.21 0.14 0.018 0.082 0.036 0.005 0.014	0.20 0.25 0.091 0.019 0.091 0.033 0.10 0.015	0.23 0.32 0.11 0.023 0.092 0.045 0.33 0.017	0.21 0.26 0.11 0.020 0.088 0.038 0.15 0.015	0.24 0.30 0.13 0.023 0.10 0.044 0.17 0.018	155 196 85 15 66 28 108	27% 53% 56% 35% 16% 40% 285% 27%	0.06 0.14 0.06 0.007 0.014 0.015 0.41 0.004	12% 9% 42% 19% 12% 59%
ulfur	2,290	2,327	2,342	2,320	2,657	1.73E+06	3%	67	0.003%

TABLE 4-11

EPA METHOD 29 MAJOR ELEMENT TEST RESULTS

NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM – STACK

AUGUST 1996

Test No.	1-MTLS-S		STK 3-MTLS	-STK	AVERAC	E		Tainty	Avg. Blank
Date	8/7/96	8/8/96	8/9/96			-	(@93	%CI	Correction
Pitot Flow Rate, dscf	ua 358,667	358, <i>7</i> 79	362,692						% of Sample
Sampic Volume, dsci	241.79	253.28	254.55						Value
Fuel Factor, dscf/10 ⁶	Bt 13,157	13,087	13,329						
O ₂ , %	5.66	5.52	5.76						
CO ₂ , %	13.81	13.57	13.67						
H ₂ O, %	14.4	14.8	14.3 .						
Element	mg/Nm³	mg/Nm 1	mg/Nm³	mg/Nm³	ib/hr	16/10 ¹² Btu	%	mg/Nm	1
Aluminum ·	0.078	0.079	0.082	0.080	0.10	61	7%	0.005	23%
Calcium	0.37	0.32	0.32	0.34	0.42	259	20%	0.07	6%
Íron	0.005	0.035	0.064	0.035	0.044	27	210%	0.073	71%
Magnesium	0.13	0.15	0.14	0.14	0.17	104	18%	0.02	3%
Phosphorus	0.019	0.019	0.022	0.020	0.025	15	20%	0.004	36%
•	D< 0.05Z 1	ND< 0.049	ND< 0.049	ND< 0.050	ND< 0.063	ND< 38		••	**
Sodium	0.49	0.06	0.00	0.18	0.23	141	359%	0.66	59%
Titanium	0.008	0.009	800.0	800.0	0.010	6.3	14%	0.001	 .
Sulfur	190	122	152	155	194	1.19E+05	54%	84	0.04%

Conclusions:

The ESP was effective at removing trace metals found primarily in the solid-phase from the flue gas stream with an average removal efficiency of 99.7%. Major ash elements were effectively removed by the ESP at an average efficiency of 99.9%. The FGD removed trace metals at an average removal efficiency of 36.0%, and major elements at an efficiency of 62.6%. The ESP removal efficiency for mercury was 17% and the FGD removal efficiency was 60%. With the exception of selenium, ESP inlet trace and major element results are in good agreement with coal input levels.

From comparisons with coal input and flyash levels, selenium results for the ESP inlet and ESP outlet are severely biased low. Severe negative matrix interferences from the high levels of sulfur found in the ESP inlet and ESP outlet samples tremendously hindered their analyses for selenium. It is now believed that sulfur interferences are the main source for the low biases associated with the selenium analytical results for Milliken Unit 2. Given the low levels of sulfur contained in the stack EPA Method 29 samples and the lack of matrix interferences encountered during analysis, the stack selenium results are considered valid.

4.4 HEXAVALENT CHROMIUM

Hexavalent chromium results are presented on Table 4-12. Reported results show that the ESP and FGD combined to remove hexavalent chromium from the flue gas stream at an efficiency of 26%. ESP inlet Cr⁶⁺ concentrations amounted to 0.1% of EPA Method 29 total chromium concentrations, and 25% of calculated gaseous chromium concentrations based on 99.5% of the total chromium existing in the solid-phase. Stack Cr⁶⁺ levels are 4.2 times higher than total chromium levels determined from the EPA 29 train. Since the caustic limestone slurry should collect soluble Cr⁶⁺ found in the flue gas entering the FGD absorber module and the acidic nature of FGD absorber module chemistry (due to large amounts of SO₂ passing through) should convert any uncollected Cr⁶⁺ to Cr³⁺, the expected stack level of hexavalent chromium is zero. This points to sample contamination as a reasonable explanation for higher hexavalent chromium emissions at the stack compared to total chromium. As a result, the combined ESP/FGD Cr⁶⁺ removal efficiency is most likely understated.

All sample results were reported well above analytical detection levels, and the reagent blank was negligible.



TABLE 4-12
HEXAVALENT CHROMIUM TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Parameter			ESP INLET			
	1-CR-IN	2-CR-IN	3-CR-IN	AVERAGE	Unc	ertainty
Date		_				95%CI
Pitot Flow Rate, dscfm	8/12/96	8/13/96	8/13/96			
Sample Volume, dscf	324,097	318,111	325,275	322,494		
Fuel Factor, dscf/10 ⁶ Btu	68.88	69.44	70.59	69.63		
O ₂ , %	13,276	12.622	12,887	12,928		
_	5.60	5.32	5.64	5.52		
CO ₂ , %	13.66	14.21	13.84	13.90		
H ₂ 0, %	9.4	8.8	8.5	8.9		
Hexavalent Chromium						(ug/Nm³)
ug/Nm ³	1.48					
lb/hr		1.14	0.76	1.13	79%	0.89
lb/10 ¹² Btu	0.0017	0.0013	0.0009	0.0013		
10/10 Btu	1.14	0.84	0.57	0.85		
Parameter			STACK			
	1-CR-STK	2-CR-STK	3-CR-STK	AVERAGE	Unce	rtainty
				···		5%CI
Date	8/12/96	8/13/96	8/13/96			
Pitot Flow Rate, dscfm*	342,528	328,348	351,432	340,769		
Sample Volume, dscf	103.47	108.17	106.56	106.06		
Fuel Factor, dscf/10 ⁶ Btu	13,139	12,557	12,630	12,775		
O ₂ , %	5.44	5.24	5.33	5.34		
CO ₂ , %	13.80	14.28	14.12	14.07		
H ₂ 0, %	13.6	13.5	14.6	13.9		
Hexavalent Chromium						(ug/Nm ³)
ug/Nm ³	1.00					
ug/Nm ⁻ lb/hr	1.09	0.77	0.68	0.84	64%	0.54
	0.0013	0.0009	0.0008	0.0010		
lb/10 ¹² Btu	0.83	0.56	0.50	0.63		_
Cr ⁶⁺ ESP/FGD Removal Efficiency	27%	33%	13%	26%		

^{*}Stack pitot flow rates for hexavalent chromium tests taken from concurrent multi-point tests.

Note: Hexavalent chromium reagent blank levels of 0.17-0.20 ug for the ESP inlet samples and 0.11-0.14 ug for the stack samples were subtracted from sample values.

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Conclusions:

Reported hexavalent chromium results show that the ESP and FGD combined to remove hexavalent chromium from the flue gas stream at an efficiency of 26%. This efficiency is most likely understated since the hexavalent chromium level at the stack was 4.2 times higher than the total chromium value from the EPA Method 29 sample train. FGD absorber module chemistry should either completely collect soluble Cr⁶⁺ or convert it to Cr³⁺. In either case, stack hexavalent chromium emissions should approach zero, suggesting sample contamination as a significant source of stack hexavalent chromium emissions.

4.5 TOTAL PARTICULATE/ANION

This section presents total particulate, and solid, gaseous, and total chloride, fluoride and sulfur flue gas results.

4.5.1 Total Particulate

Table 4-13 presents the particulate results for all three sample locations. An average ESP inlet particulate level of 6.35 lb/10⁶Btu corresponds to an average ESP outlet result of 0.007 lb/10⁶Btu and gives the ESP a removal efficiency of 99.88%. This ESP efficiency resulted in particulate concentrations that are approximately 10 times lower than those measured during the May 1994 Unit 2 baseline test program where the ESP was found to be 98.95% efficient. ESP performance tests conducted by CONSOL on Unit 2 in October of 1995 after the upgrades to the ESP were completed found a removal efficiency of 99.90% which agrees well with the removal rate measured during this test program. A 38% variability in ESP inlet particulate values may be due to sootblowing during the test. Unit 2 sootblowing was conducted normally during this test program triggered automatically by pressure differentials. There was no attempt made to coordinate the sampling and sootblowing schedules. Ash mass balance results confirms ESP inlet particulate levels.

The average stack particulate level of 0.014 lb/10⁶Btu is two times higher than the ESP outlet value. Higher FGD outlet versus inlet particulate levels are not uncommon due to the likelihood of fugitive limestone emissions. Higher ESP outlet and stack uncertainties are due to the low levels of particulate measured at these locations.

4.5.2 Anions

Anion results for the ESP inlet, ESP outlet and stack are given on Tables 4-14, 4-15 and 4-16. For the ESP inlet, flyash sulfur concentration values were used instead of the those

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TABLE 4-13
PARTICULATE RESULTS SUMMARY
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

		ESP INLET	LET			ESP (ESP OUTLET			STACK	CK	
Test Number	I-PM/AN-IN	I-PM/AN-IN 2-PM/AN-IN 3-PM	3-PM/AN-IN	Average 1-	Average 1-PM/AN-OUT 2-PM/AN-OUT 3-PM/AN-OUT	M/AN-OUT 3-1	PM/AN-OUT	Average	Average 1-PM/AN-STK 2-PM/AN-STK 3-PM/AN-STK	-PM/AN-STK	PM/AN-STK	Average
Date	96/L/8	96/8/8	96/6/8		96/L/8	96/8/8	96/6/8		96/L/8	96/8/8	96/6/8	9
Pitot Flow Rate, dscfm	319,669	344,157	329,486		325,833	336,795	341,319		336,350	334.520	331.279	
Sample Volume, dscf	10.69	150.44	140.68		152.52	147.31	147.65		141.02	142.43	143.22	
Fuel Factor, dscf/106Btu	13,157	13,096	13,311		12,919	13,164	12,676		13,252	13,079	13,329	
0,%	9.66	5.53	5.74		5.38	19'5	4.98		5.77	5.51	5.76	
CO3,%	13.84	13.58	13.70		14.09	13.51	14.38		. 13.74	13.60	13.68	
H ₂ O,%	9.2	8.0	ec.		8.7	8.4	8.4		14.1	14.4	15.5	
Grain loading, gr/dscf	2.9	3.4	3.9	3.4	0.0021	0.0074	0.0025	0.0040	0.0070	0.0111	0.0035	0.0072
Part. Conc., mg/Nm³	7,051	8,290	9,489	8,277	5.1	18.2	6.1	8.6	17.2	27.2	8.7	17.7
Mass Emissions, 1b/hr	7,867	856'6	10,912	6,579	5.8	21.4	7.2	11.5	20.2	31.7	10.0	20.6
Emission Factor, lb/10 ⁶ Btu	5.40	6.32	7.35	6.35	0.004	0.014	0.004	0.007	0.013	0.021	0.007	0.014
ESRRemoval Efficiency, %	*				99.93%	%81.66	99.94%	99.88%				
ncerpany @ 95% Cl, % Uncertainty @ 95% Cl, lb/10°Btu	% b/10 ⁶ Btu			38%				189%				128% 0.017

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TABLE 4-14
ANION TEST RESULTS SUMMARY
NYSEG POST-RETROFIT TEST PROGRAM -- ESP INLET
AUGUST 1996

Test Number	I-PM/AN-IN	2-PM/AN-IN	3-PM/AN-IN		AVERAG	E	Unce	rtainty
Dațe	8/7/96	8/8/96	8/9/96				@95	5%CI
Pitot Flow Rate, dscfm	319,669	344,157	329,486					
Sample Volume, dscf	69.01	150.44	140.68					
Fuel Factor, dscf/10 ⁶ Btu	13,157	13,096	13,311					
O ₂ , %	5.66	5.53	5.74					
CO ₂ ,%	13.84	13.58	13.70					
H ₂ O,%	9.2	8.0	8.8					
Parameter	ppm	ppm	ppm	ppm	lb/hr	lb/10 ¹² Btu	%	ppm
Chlorine (as Cl')								
Solid Fraction	0.56	0.13	5.1	1.9	3.5	2,362		
Gaseous Fraction	52	53	50	52	95	62,828	10%	5.1
Total	53	54	55	54	98	65,190	3.9%	2.1
Fluorine (as F')								
Solid Fraction	0.95	0.88	2.6	1.5	1.5	969		
Gaseous Fraction	8.4	10	7.6	8.6	8.4	5,592	32%	2.7
Total	9.4	11	10	10	10	6,561	17%	1.7
Sulfur								
Solid Fraction(1)	24	26	28	26	43	28,372		
Gaseous Fraction(2)	1,686	1.743	1,671	1,700	2,806	1.84E+06	6%	94
Total ⁽²⁾	1,710	1,769	1,699	1,726	2,849	1.87E+06	5%	94

Notes:

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⁽¹⁾ Results taken from sulfur flyash concentration levels corrected to total solids catch amounts in sample train.

⁽²⁾ Sulfate results from the 3% peroxide fraction yeilded SO_2 levels 65-75% below expected levels given fuel input values. Total sulfur results from EPA Method 29 samples used instead. Gaseous fraction determined by difference.

TABLE 4-15
ANION TEST RESULTS SUMMARY
NYSEG POST-RETROFIT TEST PROGRAM -- ESP OUTLET
AUGUST 1996

Test Number	1-PM/AN-OU	Γ 2-PM/AN-OUT	3-PM/AN	I-OUT	AVERA	GE	Unce	rtainty
Date	8/7/96	8/8/96 .	8/9/96				@95	%CI
Pitot Flow Rate, dscfm	325,833	336.795	341,319					
Sample Volume, dscf	152.52	147.31	147.65					
Fuel Factor, dscf/106Btu	12.919	13,164	12,676					
O ₂ , %	5.38	5.61	4.98					
CO ₂ ,%	14.09	13.51	14.38					
H ₂ O,%	8.7	8.4	8.4					
Parameter	ppm	ppm	ppm	ppm	lb/hr	lb/10 ¹² Btu	%	ppm
Chlorine (as Cl')								
Solid Fraction	0.001 ND	< 0.003	0.003	ND< 0.003	ND< 0.005	ND< 3.1		
Gaseous Fraction	51	56	57	55	101	65,157	14%	7.7
Total	51	56	57	55	101	65,159	14%	7.7
Fluorine (as F')	i.							
Solid Fraction	0.09	0.13	0.11	0.11	0.11	69		
Gaseous Fraction	8.8	10	11	10	10	6,423	33%	3.4
Total	8.9	10	12	10	10	6,492	33%	3.4
Sulfur								
Solid Fraction	0.4	2.0	0.7	1.0	1.7	1,126		
Gaseous Fraction(1)	1,602	1,627	1,639	1,623	2,655	1.72E+06	2.8%	46
Total ⁽¹⁾	1,603	1,629	1,639	1,624	2,657	1.73E+06	2.9%	47

Note: (1) Sulfate results from the 3% peroxide fraction yeilded SO_2 levels 65-75% below expected levels given fuel input values. Total sulfur results from EPA Method 29 samples used instead. Gaseous fraction determined by difference.



TABLE 4-16
ANION TEST RESULTS SUMMARY
NYSEG POST-RETROFIT TEST PROGRAM -- STACK
AUGUST 1996

Test Number	1-PM/A	N-STK 2-I	M/AN-STK	3-PM/AN	N-STK	AVERA	GE	Unac	
Date	8/7/96		1/96	8/9/96		AVEIG	GL .	_	rtainty
Pitot Flow Rate, dsc	fm 336,350	334	4,520	331,279				(4)9	5%CI
Sample Volume, dsc	f 141.02		2.43	143.22					
Fuel Factor, dscf/106	Btu 13.303	13.	078	13,294					
O ₂ , %	5.77	5.5	1	5.76					
CO ₂ ,%	13.74	13.	60	13.68					Sec.
H ₂ O,%	14.1	14.	4	15.5					
Parameter	ppm	ppm	<u> </u>	ppm	ppm	lb/hr	lb/10 ¹² Btu	%	ppm
Chlorine (as Cl7)							10/10 Diu		ppm
Solid Fraction	ND< 0.003	ND< 0.0	03 ND<	0.003	ND< 0.003	ND< 0.005	ND< 3.3		
Gaseous Fraction	0.37	0.3)	0.30	0.33	0.60	396	32%	0.1
Total	0.37	0.3)	0.30	0.33	0.60	398	31.5%	0.1
Fluorine (as F')									
Solid Fraction	0.01	ND< 0.0	İ	0.01	0.01	0.01	5.3		
Gaseous Fraction	0.19	0.10)	0.07	0.12	0.12	80	129%	0.2
Total	0.21	0.11	l	0.08	0.13	0.13	85	127%	0.2
Sulfur									
Solid Fraction	1.9	2.8		1.0	1.9	3	2,082		
Gaseous Fraction(1)	131	83		105	106	. 191	1.17E+05	56%	60
Total ⁽¹⁾	133	86		106	108	194	1.17E+05 1.19E+05	54%	60 59

Note: (1) To be consistent with the ESP inlet and outlet, EPA Method 29 total sulfur results used for the stack. Gaseous fraction determined by difference.



determined from the particulate/anion front-half solids by a water extraction. Differences in the two sets of results indicate that some of the sulfur species present in the ash are not water soluble. For the ESP inlet and outlet, gaseous sulfur concentrations in the 3% peroxide fractions amounted to only 65-70% of the gaseous sulfur levels expected from coal input values. It appears that the peroxide impingers became over-saturated during the four-hour sampling time at 1500 ppm SO₂. Valid total sulfur results from the EPA Method 29 sample trains were used in place of the erroneous ESP inlet and outlet sulfur data, and in place of the stack data for consistency purposes. Gaseous sulfur levels were determined from the difference between solid sulfur and total sulfur results.

As presented on Table 4-1, the ESP was only effective at removing solid-phase anion species with removals of >99.9%, 92.8% and 96.0% for solid chloride, fluoride and sulfur, respectively. The gaseous fraction contributed 96%, 85% and 98% to total ESP inlet chloride, fluoride and sulfur levels, respectively. This increases to 99-100% for the ESP outlet, and then drops somewhat to 94-99% for the stack. The FGD was effective at removing chloride from the flue gas with an efficiency of 99.4%. FGD removal rates for fluoride were 92.3% for the solid fraction and 98.7% for total fluoride. Sulfur FGD removal efficiency averaged 93.1%. ESP inlet and outlet sulfur levels agree well (±5%) with coal sulfur input values.

Conclusions:

The ESP removal efficiency for filterable particulate was 99.88%. ESP and coal mill upgrades for the post-retrofit test program reduced ESP outlet particulate concentrations by almost a factor of 10 when compared to pre-retrofit levels. Stack particulate emissions averaged 0.007 gr/dscf or 0.014 lb/106Btu. Chloride, fluoride and sulfur were found predominantly in the gaseous phase. The FGD was effective at removing chloride, fluoride and sulfur from the flue gas with average removal efficiencies of 99.4%, 98.7% and 93.1%, respectively. Mass balance results confirm particulate and anion flue gas concentration levels.

4.6 SEMI-VOLATILE ORGANICS

4.6.1 Polycyclic Aromatic Hydrocarbons

The PAH test results are presented in the following tables:

Table 4-17: Summary of PAH Test Results

Table 4-18: PAH Test Results -- ESP Inlet

Table 4-19: PAH Test Results -- ESP Outlet

Table 4-20: PAH Test Results -- Stack

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TABLE 4-17 SUMMARY OF PAH TEST RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM AUGUST 1996

Species	PAI	H Emissions, ug/N	m³	Field	Blank Levels, ug/	Nm³
	ESP INLET	ESP OUTLET	STACK	ESP INLET	ESP OUTLET	STACK
Naphthalene	9.5	13	14	0.47	0.44	0.41
2-Methylnaphthalene	0.038	0.038	0.31	0.012	0.011	0.01
Acenaphthylene	ND< 0.003	0.004	ND< 0.008	0.006	0.006	0.00
Acenaphthene	0.020	ND< 0.079	ND< 0.012	ND< 0.039	ND< 0.036	0.00
Fluorene	ND< 0.034	ND< 0.063	ND< 0.046	ND< 0.033	ND< 0.030	ND< 0.00
Phenanthrene	, 0.004	ND< 0.030	0.13	0.006	0.006	0.003
Anthracene	0.027	0.019	ND< 0.004	0.012	0.000	0.00
Fluoranthene	ND< 0.003	ND< 0.003	0.010	ND< 0.003	ND< 0.003	ND< 0.003
Pyrene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003
Benz(a)anthracene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003
Chrysene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003
Benzo(b)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.005
Benzo(k)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003
Benzo(e)pyrene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.006	ND< 0.006	ND< 0.005
Benzo(a)pyrene	ND< 0.006	ND< 0.006	ND< 0.005	ND< 0.006	ND< 0.006	ND< 0.005
Perylene	ND< 0.008	ND< 0.006	ND< 0.008	0.009	0.008	ND< 0.005
ndeno(1,2,3-cd)pyrene	ND< 0.006	ND< 0.006	ND< 0.005	ND< 0.006	ND< 0.006	ND< 0.005
Dibenzo(a,h)anthracene	ND< 0.009	ND< 0.008	ND< 0.008	ND< 0.009	ND< 0.008	ND< 0.008
Benzo(g,h,i)perylene	ND< 0.009	ND< 0.008	ND< 0.008	ND< 0.009	ND< 0.008	ND< 0.008

ND< - species not detected

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TABLE 4-18
POLYCYCLIC AROMATIC HYDROCARBON TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP INLET
AUGUST 1996

Species	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu	%	ug/Nm
H ₂ O, %	1.8	7.8	7.9					
CO ₂ , %	14.00	13.81	14.17					
O ₂ , %	5.40	5.73	5.15					
Fuel Factor, dscf/10 ⁶ Btu	13.004	13.390	. 12.486					
Sample Volume, dscf	124.74	131.80	127.23					
Pitot Flow Rate, dscfm	313,044	319.429	311,472					570 C.I.
Date	8/12/96	8/12/96	8/13/96	 			-	95% C.I.
Test No.	1-SV-IN	2-SV-IN	3-SV-IN		AVERAGE		Unc	ertainty

Species	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu	%	ug/Nm³
Naphthalene	7.6	12	9.5	9.5	1.0E-02	7.2	51%	4.8
2-Methylnaphthalene	0.046	0.032	0.036	0.038	4.1E-05	0.028	47%	0.018
Acenaphthylene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002		0.010
Acenaphthene	0.033	ND< 0.012	0.021	0.020	2.2E-05	0.015	172%	0.034
Fluorene	ND< 0.091	ND< 0.006	ND< 0.006	ND< 0.034	ND< 3.7E-05	ND< 0.026		0.054
Phenanthrene	ND< 0.003	0.009	0.003	0.004	4.8E-06	0.003	213%	0.009
Anthracene	0.043	0.035	0.003	0.027	2.9E-05	0.020	195%	0.052
Fluoranthene	0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002		
Pyrene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002		
Benz(a)anthracene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002		
Chrysene	ND< 0.003	ND< 0.003	0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002		
Benzo(b)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002	**	
Benzo(k)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002		
Benzo(e)pyrene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.3E-06	ND< 0.002		
Benzo(a)pyrene	ND< 0.006	ND< 0.006	ND< 0.006	ND< 0.006	ND< 6.5E-06	ND< 0.004		
Perylene	ND< 0.006	ND< 0.012	ND< 0.006	ND< 0.008	ND< 8.6E-06	ND< 0.006		
Indeno(1,2,3-cd)pyrene	ND< 0.006	ND< 0.006	ND< 0.006	ND< 0.006	ND< 6.5E-06	ND< 0.004	••	••
Dibenzo(a.h)anthracen	ND< 0.009	ND< 0.009	ND< 0.009	ND< 0.009	ND< 9.8E-06	ND< 0.007		
Benzo(g,h,i)perylene	ND< 0.009	ND< 0.009	ND< 0.009	ND< 0.009	ND< 9.8E-06	ND< 0.007		
Total PAH	7.8	12	9.6	9.7	1.1E-02	7.3	49%	4.74
Total PAH w.o./	0.20	0.12	0.10	0.14	1.5E-04	0.10	100%	0.14
Naphthalene				-	1.52 04	0.10	100/0	0.17

ND< - species was not detected in the sample.



TABLE 4-19
POLYCYCLIC AROMATIC HYDROCARBON TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP OUTLET
AUGUST 1996

Test No.	1-SV-OUT	2-SV-OUT	3-SV-OU	AVERAGE	Uncertainty
Date	8/12/96	8/12/96	8/13/96		@,95% C.I.
Pitot Flow Rate, dscfm	321,952	320,301	321,047		(a) 7376 C.1.
Sample Volume, dscf	136.69	138.35	136.90		
Fuel Factor, dscf/106Btu	12,216	12,743	. 11,789		
O ₂ , %	4.40	4.96	4.22		
CO ₂ , %	14.90	14.51	15.00		
H ₂ O, %	7.8	7.7	8.2		

Species	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu	%	ug/Nm ³
Naphthalene	14	13	13	13	1.5E-02	9.4	15%	2.0
2-Methylnaphthalene	0.069	0.019	0.025	0.038	4.2E-05	0.027	180%	0.068
Acenaphthylene	0.003	0.005	0.003	0.004	4.1E-06	0.027	106%	
Acenaphthene	ND< 0.030	ND< 0.079	0.006	ND< 0.079	ND< 9.0E-05	ND< 0.057	10076	0.004
Fluorene	ND< 0.072	ND< 0.093	ND< 0.025	ND< 0.063	ND< 7.1E-05	ND< 0.037		
Phenanthrene	0.011	ND< 0.030	0.011	ND< 0.030	ND< 3.4E-05	ND< 0.022		_
Anthracene	0.022	0.030	0.006	0.019	2.2E-05	0.014	162%	0.031
Fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		0.051
Pyrene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benz(a)anthracene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Chrysene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(b)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(k)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(e)pyrene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(a)pyrene	ND< 0.006	ND< 0.005	ND< 0.006	ND< 0.006	ND< 6.2E-06	ND< 0.004		
Perylene	ND< 0.006	ND< 0.005	ND< 0.006	ND< 0.006	ND< 6.2E-06	ND< 0.004		
Indeno(1,2,3-cd)pyrene	ND< 0.006	ND< 0.005	ND< 0.006	ND< 0.006	ND< 6.2E-06	ND< 0.004		
Dibenzo(a,h)anthracen	ND< 0.008	ND< 0.008	ND< 0.008	ND< 0.008	ND< 9.3E-06	ND< 0.004		
Benzo(g,h,i)perylene	ND< 0.008	ND< 0.008	ND< 0.008	ND< 0.008	ND< 9.3E-06	ND< 0.006		
Total PAH	14	13	13	13	1.5E-02	9.5	15%	2.02
Total PAH w.o./	0.18	0.18	0.09	0.15	1.7E-04	0.11	89%	0.13
Naphthalene				02	1.72-04	0.11	09/0	0.13

ND< - species was not detected in the sample.

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TABLE 4-20
POLYCYCLIC AROMATIC HYDROCARBON TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- STACK
AUGUST 1996

Test No.	1-SV-ST	K 2-SV-ST	K 3-SV-STK		AVERAGE		Unc	ertainty
Date	8/12/96	8/12/96	8/13/96				_	5% C.I.
Pitot Flow Rate, dscfm	343.069	341,987	328,348					
Sample Volume, dscf	149.50	144.29	144.92		•			
Fuel Factor, dscf/106B	tu 13,046	13,434	12,352					
O ₂ , % .	5.45	5.78	4.98					
CO ₂ , %	13.95	13.76	14.32					
H ₂ O. %	14.3	14.6	14.3					
Species	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu	%	ug/Nm³
Naphthalene	14,	14	13	14	1.6E-02	10.3	14%	2.0
2-Methylnaphthalene	0.30	0.32	0.31	0.31	3.7E-04	0.23	5%	0.01
Acenaphthylene	ND< 0.008	ND< 0.008	ND< 0.008	ND< 0.008	ND< 9.2E-06	ND< 0.006		
Acenaphthene	ND< 0.015	ND< 0.016	ND< 0.005	ND< 0.012	ND< 1.4E-05	ND< 0.009		
Fluorene	ND< 0.046	ND< 0.055	ND< 0.037	ND< 0.046	ND< 5.4E-05	ND< 0.035		
Phenanthrene	0.14	0.16	0.081	0.13	1.5E-04	0.098	82%	0.11
Anthracene	ND< 0.005	ND< 0.005	ND< 0.003	ND< 0.004	ND< 5.1E-06	ND< 0.003		
Fluoranthene	0.013	0.013	0.005	0.010	1.2E-05	0.008	106%	0.011
Pyrene	0.005	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002	-	
Benz(a)anthracene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Chrysene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(b)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(k)fluoranthene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(e)pyrene	ND< 0.003	ND< 0.003	ND< 0.003	ND< 0.003	ND< 3.1E-06	ND< 0.002		
Benzo(a)pyrene	ND< 0.005	ND< 0.005	ND< 0.005	ND< 0.005	ND< 6.1E-06	ND< 0.004		
Perylene	ND< 0.008	ND< 0.008	0.005	ND< 0.008	ND< 9.2E-06	ND< 0.006		
Indeno(1,2,3-cd)pyrene	ND< 0.005	ND< 0.005	ND< 0.005	ND< 0.005	ND< 6.1E-06	ND< 0.004		
Dibenzo(a,h)anthracene	ND< 0.008	ND< 0.008	ND< 0.008	ND< 0.008	ND< 9.2E-06	ND< 0.006		
Benzo(g,h,i)perylene	ND< 0.008	ND< 0.008	ND< 0.008	ND< 0.008	ND< 9.2E-06	ND< 0.006		
Total PAH	15	15	13	- 14	1.7E-02	11	15%	2.10
Total PAH w.o./	0.52	0.56	0.45	0.51	6.0E-04	0.39	26%	0.13
Naphthalene								-

ND< - species was not detected in the sample.



Only naphthalene and 2-methylnaphthalene at all three sample locations, phenanthrene at the stack, anthracene at the ESP inlet and outlet, and fluoranthene at the stack were detected at levels two times higher than the analytical detection limit. These species were also the only ones found notably above field blank values. Only 5 out of 19 total species were detected at the ESP inlet, and only 4 species were detected at the ESP outlet and stack.

Only naphthalene, 2-methylnaphthalene, and anthracene were detected in all three replicates at the ESP inlet. For the ESP outlet and stack, average species reported above the detection limit were detected in all three replicates. Total PAH levels excluding naphthalene but including non-detected species divided by two amounts to 0.14 ug/Nm³ for the ESP inlet, 0.15 ug/Nm³ for the ESP outlet, and 0.51 ug/Nm³ for the stack.

4.6.2 PCDD/PCDF

The results of the PCDD/PCDF tests are presented in the following tables:

Table 4-21: Summary of PCDD/PCDF Test Results

Table 4-22: PCDD/PCDF Test Results -- ESP Inlet

Table 4-23: PCDD/PCDF Test Results -- ESP Outlet

Table 4-24: PCDD/PCDF Test Results -- Stack

Table 4-25: Average PCDD/PCDF Toxic Equivalent Results

Of the 17 total 2,3,7,8-substituted isomers, only 7 were reported above the detection limit at the ESP inlet, and only 5 of these were detected in all three replicates. At the ESP outlet, 5 isomers were detected of which 4 were found in every replicate. For the stack, 7 isomers were detected and only 4 were found in every replicate. Only 123478 HxCDD and OCDD were detected in every replicate at each location. No dioxin/furan isomer, however, was detected at levels greater than twice the field blank. Total PCDD/PCDF levels were comparable with field blank results.

Toxic equivalent concentrations calculated using EPA methodology and their 1989 NATO toxic equivalency factors show total 2378 TCDD equivalent concentrations to be at 0.0053 ng/Nm₃ at the inlet, 0.0061 ng/Nm³ at the outlet, and 0.0055 ng/Nm³ at the stack. If only the detected isomers are considered, toxic equivalent concentrations drop to 0.0019 at the inlet, 0.0038 at the outlet, and 0.0041 at the stack.

Conclusions:

For PAH emissions, only naphthalene, 2-methylnaphthalene, phenanthrene, and fluoranthene were measured at the stack at levels two times higher than the analytical detection

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TABLE 4-21 SUMMARY OF PCDD/PCDF RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM AUGUST 1996

Species		PCDF Emissions.	, ng/Nm³	Fiel	d Blank Levels, n	r/Nm³
	ESP INLET	ESP OUTLET	STACK	ESP INLET	ESP OUTLET	STACK
						Jiitell
2378-TCDD	ND< 0.0020	0.0025	0.0023	0.0028	0.0026	0.0026
12378 PeCDD	0.0018	0.0017	ND< 0.0017	0.0017	0.0016	0.0016
123478 HxCDD	0.0049	0.0048	0.0042	0.0062	0.0058	0.0054
123678 HxCDD	ND< 0.0006	ND< 0.0007	ND< 0.0008	ND< 0.0005	ND< 0.0004	ND< 0.0005
123789 HxCDD	ND< 0.0009	ND< 0.0010	ND< 0.0011	ND< 0.0007	ND< 0.0006	ND< 0.0007
1234678 HpCDD	0.0028	0.0012	ND< 0.0028	0.0033	0.0030	0.0021
OCDD	0.0122	0.0048	0.0086	0.0151	0.0141	0.0021
2378 TCDF	ND< 0.0024	ND< 0.0010	0.0028	ND< 0.0005	ND< 0.0005	ND< 0.0005
12378 PeCDF	0.0011	ND< 0.0010	ND< 0.0008	0.0007	0.0006	0.0006
23478 PeCDF	ND< 0.0014	ND< 0.0012	0.0013	0.0005	0.0005	0.0007
123478 HxCDF	ND< 0.0012	ND< 0.0044	ND< 0.0009	ND< 0.0007	ND< 0.0007	ND< 0.0007
123678 HxCDF	ND< 0.0007	ND< 0.0013	ND< 0.0005	ND< 0.0004	ND< 0.0004	ND< 0.0007
234678 HxCDF	ND< 0.0012	ND< 0.0011	ND< 0.0009	ND< 0.0007	ND< 0.0007	ND< 0.0004 ND< 0.0007
123789 HxCDF	0.0039	ND< 0.0066	0.0042	0.0047	0.0044	0.0041
1234678 HpCDF	ND< 0.0026	ND< 0.0011	ND< 0.0014	ND< 0.0013	ND< 0.0012	ND< 0.0009
1234789 HpCDF	ND< 0.0017	ND< 0.0012	ND< 0.0018	ND< 0.0002	ND< 0.0012	ND< 0.0009 ND< 0.0007
OCDF	0.0025	ND< 0.0015	0.0032	0.0033	0.0030	0.0020
Total TCDD	0.0074	0.0037	0.0023	0.0028	0.0026	0.0026
Total PeCDD	0.0018	0.0047	ND< 0.0017	0.0017	0.0016	0.0020
Total HxCDD	0.0048	0.0113	0.0029	0.0041	0.0039	0.0010
Total HpCDD	0.0045	0.0012	ND< 0.0028	0.0053	0.0059	0.0039
Total TCDF	ND< 0.0052	0.0025	0.0053	ND< 0.0005	ND< 0.0005	0.0007
Total PeCDF	0.0021	0.0013	0.0028	0.0012	0.0011	0.0007
Total HxCDF	0.0053	ND< 0.0099	0.0033	0.0036	0.0033	0.0013
otal HpCDF	ND< 0.0058	ND< 0.0012	ND< 0.0016	0.0022	- 0.0020	0.0007
Total PCDD	0.031	0.026	0.017	0.029	0.027	0.020
otal PCDF	0.015	0.011	0.015	0.010	0.010	0.028
Total PCDD/PCDF	0.046	0.036	0.032	0.040	0.037	0.028



TABLE 4-22 PCDD / PCDF TEST RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP INLET **AUGUST 1996**

Test No.	1-SV-IN	2-SV-IN	3-SV-IN	AVERAGE	Uncertainty
Date	8/12/96	8/12/96	8/13/96		@ 95% C.I.
Pitot Flow Rate, dscfm	313,044	319,429	311,472	•	<u> </u>
Sample Volume, dscf	124.74	131.80	127.23		
Fuel Factor, dscf/106Btu	13,004	13,390	12,486		
O ₂ , %	5.40	5.73	5.15		
CO ₂ , %	14.00	13.81	14.17		
H ₂ O, %	8.1	7.8	7.9		

Species	ng/Nm³	ng/Nm³	ng/Nm³	ng/Nm³	lb/hr	lb/10 ¹² Btu	%	ng/Nm³
2378-TCDD	ND< 0.0020	ND< 0.0009	0.0022	ND< 0.0020	ND< 2.1E-09	ND< 1.5E-06		
12378 PeCDD	0.0022	0.0017	0.0016	0.0018	2.0E-09	1.4E-06	41%	0.0007
123478 HxCDD	0.0052	0.0052	0.0045	0.0049	5.4E-09	3.7E-06	20%	0.0007
123678 HxCDD	0.0012	ND< 0.0006	ND< 0.0006	ND< 0.0006	ND< 7.2E-10	ND< 4.9E-07	2070	0.0010
123789 HxCDD	0.0013	ND< 0.0009	ND< 0.0008	ND< 0.0009	ND< 9.8E-10	ND< 6.7E-07		
1234678 HpCDD	0.0036	0.0013	0.0036	0.0028	3.1E-09	2.1E-06	117%	0.0033
OCDD	0.0100	0.0043	0.0223	0.0122	1.3E-08	9.0E-06		0.0229
2378 TCDF	0.0026	ND< 0.0024	ND< 0.0008	ND< 0.0024	ND< 2.8E-09	ND< 1.9E-06		
12378 PeCDF	0.0021	0.0009	ND< 0.0007	0.0011	1.2E-09	8.5E-07	194%	0.0022
23478 PeCDF	ND< 0.0014	0.0009	ND< 0.0007	ND< 0.0014	ND< 1.5E-09	ND< 1.0E-06		
123478 HxCDF	0.0024	ND< 0.0012	ND< 0.0009	ND< 0.0012	ND< 1.4E-09	ND< 9.6E-07		**
123678 HxCDF	0.0009	ND< 0.0007	ND< 0.0006	ND< 0.0007	ND< 8.1E-10	ND< 5.6E-07		
234678 HxCDF	0.0008	ND< 0.0012	ND< 0.0009	ND< 0.0012	ND< 1.4E-09	ND< 9.4E-07		
123789 HxCDF	0.0039	0.0037	0.0039	0.0039	4.2E-09	2.9E-06	7%	0.0003
1234678 HpCDF	ND< 0.0052	ND< 0.0013	ND< 0.0013	ND< 0.0026	ND< 2.8E-09	ND< 2.0E-06		
1234789 HpCDF	ND< 0.0027	ND< 0.0012	ND< 0.0011	ND< 0.0017	ND< 1.8E-09	ND< 1.3E-06		
OCDF	0.0033	ND< 0.0018	0.0033	0.0025	2.7E-09	1.9E-06	140%	0.0035
Total TCDD	ND< 0.0020	0.0190	0.0022	0.0074	8.2E-09	5.7E-06	337%	0.025
Total PeCDD	0.0022	0.0017	0.0016	0.0018	2.0E-09	1.4E-06	41%	0.0007
Total HxCDD	0.0064	0.0035	0.0045	0.0048	5.2E-09	3.6E-06	77%	0.0037
Total HpCDD	0.0067	0.0013	0.0057	0.0045	5.0E-09	3.4E-06	156%	0.0071
Total TCDF	0.0067	ND< 0.0052	0.0010	ND< 0.0052	ND< 5.9E-09	ND< 4.0E-06		
Total PeCDF	0.0021	0.0037	ND< 0.0007	0.0021	2.3E-09	1.6E-06	203%	0.0042
Total HxCDF	0.0091	0.0037	0.0030	0.0053	5.8E-09	4.0E-06	157%	0.0083
Total HpCDF	ND< 0.0058	ND< 0.0014	0.0026	ND< 0.0058	ND< 6.2E-09	ND< 4.2E-06		
Total PCDD	0.026	0.030	0.036	0.031	3.4E-08	2.3E-05	41%	0.013
Total PCDF	0.024	0.012	0.010	0.015	1.7E-08	1.2E-05	124%	0.019
Total PCDD/PCDF	0.050	0.041	0.046	0.046	5.1E-08	3.5E-05	24%	0.011

ND< - species not detected in sample.

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TABLE 4-23 PCDD / PCDF TEST RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP OUTLET **AUGUST 1996**

Test No.	I-SV-O	UT 2-SV-OU	T 3-SV-OU		AVERAGE		Unc	ertainty
Date	8/12/96	8/12/96	8/13/96				- @ 9:	5% C.I.
Pitot Flow Rate, ds	cfm 321.952	320.301	321,047					
Sample Volume, ds	cf 136.69	138.35	136.90					
Fuel Factor, dscf/10	D ⁶ Btu 12,216	12,743	11,789					
O ₂ , %	4.40	4.96	4.22					
CO ₂ , %	14.90	14.51	15.00					
H ₂ O, %	7.8	7.7	- 8.2					
•								
Species	ng/Nm³	ng/Nm³	ng/Nm³	ng/Nm³	lb/hr	lb/10 ¹² Btu	%	ng/Nm³
2378-TCDD	0.0026	0.0024	0.0025	0.0025	2.8E-09	1.8E-06	10%	0.0003
12378 PeCDD	0.0016	0.0020	0.0016	0.0017	1.9E-09	1.2E-06	38%	0.0005
123478 HxCDD	0.0047	0.0044	0.0053	0.0017	5.4E-09	3.4E-06	23%	0.0000
123678 HxCDD	ND< 0.0008	ND< 0.0006	ND< 0.0006	ND< 0.0007	ND< 7.7E-10	ND< 4.9E-07		
23789 HxCDD	ND< 0.0011	ND< 0.0009	ND< 0.0009	ND< 0.0010	ND< 1.1E-09	ND< 6.9E-07		
234678 HpCDD	0.0016	ND< 0.0012	0.0015	0.0012	1.4E-09	8.6E-07	110%	0.0014
OCDD	0.0050	0.0036	0.0058	0.0048	5.4E-09	3.4E-06	59%	0.0028
					2112			0.0020
378 TCDF	0.0018	ND< 0.0010	ND< 0.0008	ND< 0.0010	ND< 1.2E-09	ND< 7.5E-07		
2378 PeCDF	ND< 0.0010	0.0008	ND< 0.0010	ND< 0.0010	ND< 1.1E-09	ND< 7.3E-07		
3478 PeCDF	ND< 0.0010	0.0010	ND< 0.0012	ND< 0.0012	ND< 1.4E-09	ND< 8.6E-07		
23478 HxCDF	ND< 0.0009	ND< 0.0112	ND< 0.0011	ND< 0.0044	ND< 4.9E-09	ND< 3.2E-06		
23678 HxCDF	ND< 0.0005	ND< 0.0009	ND< 0.0026	ND< 0.0013	ND< 1.5E-09	ND< 9.4E-07		
34678 HxCDF	ND< 0.0009	ND< 0.0015	ND< 0.0010	ND< 0.0011	ND< 1.3E-09	ND< 8.0E-07	••	
23789 HxCDF	0.0039	ND< 0.0066	0.0033	ND< 0.0066	ND< 7.4E-09	ND< 4.7E-06		
234678 HpCDF	ND< 0.0008	ND< 0.0017	ND< 0.0008	ND< 0.0011	ND< 1.2E-09	ND< 7.8E-07		
234789 HpCDF	ND< 0.0010	ND< 0.0015	ND< 0.0011	ND< 0.0012	ND< 1.3E-09	ND< 8.4E-07		
OCDF	ND< 0.0018	ND< 0.0016	ND< 0.0011	ND< 0.0015	ND< 1.6E-09	ND< 1.1E-06		
otal TCDD	0.0026	0.0024	0.0061	0.0037	4.1E-09	2.6E-06	141%	0.0052
Total PeCDD	0.0016	0.0020	0.0105	0.0047	5.3E-09	3.3E-06	267%	0.0125
otal HxCDD	0.0033	0.0271	0.0036	0.0113	1.3E-08	8.3E-06		0.0339
otal HpCDD	0.0016	ND< 0.0012	0.0015	0.0012	1.4E-09	8.6E-07	110%	0.0014
otal TCDF	0.0058	ND< 0.0015	ND< 0.0022	0.0025	2.9E-09	1.8E-06	277%	0.0071
otal PeCDF	ND< 0.0010	0.0027	ND< 0.0011	0.0013	1.4E-09	9.2E-07	253%	0.0032
otal HxCDF	0.0086	ND< 0.0099	0.0026	ND< 0.0099	ND< 1.1E-08	ND< 7.1E-06		
Total HpCDF	ND< 0.0009	ND< 0.0019	ND< 0.0009	ND< 0.0012	ND< 1.4E-09	ND< 8.9E-07		
Total PCDD	0.014	0.036	0.027	0.026	2.9E-08	1.8E-05	105%	0.027
Total PCDF	0.016	0.010	0.005	0.011	1.6E-08	7.5E-06	131%	0.014
Total PCDD/PCDF		0.046						0.021
Total PCDD/PCDF	0.030	0.046	0.033	0.036	4.5E-08	2.6E-05	57%	

ND< - species not detected in sample.

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TABLE 4-24
PCDD / PCDF TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- STACK
AUGUST 1996

Test No.	1-SV-ST	K 2-SV-ST	K 3-SV-ST		AVERAGE			
Date	8/12/96	8/12/96	8/13/96				_	ertainty 5% C.I.
Pitot Flow Rate, dscfr	n 343,069	341,987	328,348					370 C.1.
Sample Volume, dscf	149.50	144.29	144.92					
Fuel Factor, dscf/106E	Btu 13,046	13,434	12,352					
O ₂ , %	5.45	5.78	4.98					
CO ₂ , %	13.95	13.76	14.32					
H ₂ O, %	14.3,	14.6	14.3					
Species	ng/Nm³	ng/Nm³	ng/Nm³	ng/Nm³	lb/hr	lb/10 ¹² Btu	%	ng/Nm³
2378-TCDD	0.0022	0.0026	0.0021	0.0023	2.7E-09	1.7E-06	24%	0.0006
12378 PeCDD 1	ND< 0.0017	0.0015	0.0013	ND< 0.0017	ND< 2.1E-09	ND< 1.3E-06	24/0	0.0006
123478 HxCDD	0.0041	0.0045	0.0042	0.0042	5.0E-09	3.2E-06	12%	0.0005
123678 HxCDD N	VD< 0.0011	ND< 0.0006	ND< 0.0006	ND< 0.0008	ND< 9.5E-10	ND< 6.0E-07	12/0	0.0003
123789 HxCDD N	ND< 0.0016	ND< 0.0009	ND< 0.0009	ND< 0.0011	ND< 1.3E-09	ND< 8.4F-07		

2378-TCDD	0.0022	0.0007	0.0001					
12378 PeCDD		0.0026	0.0021	0.0023	2.7E-09	1.7E-06	24%	0.0006
	ND< 0.0017	0.0015	0.0013	ND< 0.0017	ND< 2.1E-09	ND< 1.3E-06		
123478 HxCDD	0.0041	0.0045	0.0042	0.0042	5.0E-09	3.2E-06	12%	0.0005
123678 HxCDD	ND< 0.0011	ND< 0.0006	ND< 0.0006	ND< 0.0008	ND< 9.5E-10	ND< 6.0E-07		
123789 HxCDD	ND< 0.0016	ND< 0.0009	ND< 0.0009	ND< 0.0011	ND< 1.3E-09	ND< 8.4E-07		
1234678 HpCDD	ND< 0.0028	0.0023	ND< 0.0021	ND< 0.0028	ND< 3.4E-09	ND< 2.1E-06		
OCDD	0.0081	0.0066	0.0112	0.0086	1.0E-08	6.5E-06	68%	0.0059
2222								
2378 TCDF	0.0038	0.0039	ND< 0.0016	0.0028	3.4E-09	2.2E-06	155%	0.0044
12378 PeCDF	ND< 0.0006	0.0010	ND< 0.0008	ND< 0.0008	ND< 9.2E-10	ND< 5.8E-07		
23478 PeCDF	0.0016	0.0017	ND< 0.0012	0.0013	1.6E-09	1.0E-06	119%	0.0016
123478 HxCDF	ND< 0.0010	ND< 0.0008	ND< 0.0008	ND< 0.0009	ND< 1.0E-09	ND< 6.6E-07		
123678 HxCDF	ND< 0.0006	ND< 0.0005	ND< 0.0005	ND< 0.0005	ND< 6.1E-10	ND< 3.9E-07		
234678 HxCDF	ND< 0.0009	ND< 0.0008	ND< 0.0008	ND< 0.0009	ND< 1.0E-09	ND< 6.4E-07		
123789 HxCDF	0.0038	0.0045	0.0042	0.0042	4.9E-09	3.1E-06	20%	0.0008
1234678 HpCDF	ND< 0.0017	ND< 0.0013	ND< 0.0012	ND< 0.0014	ND< 1.7E-09	ND< 1.1E-06		
1234789 HpCDF	ND< 0.0023	ND< 0.0017	ND< 0.0014	ND< 0.0018	ND< 2.1E-09	ND< 1.4E-06		
OCDF	0.0053	ND< 0.0023	0.0031	0.0032	3.8E-09	2.4E-06	163%	0.0052
								0.0052
Total TCDD	0.0022	0.0026	0.0021	0.0023	2.7E-09	1.7E-06	24%	0.0006
Total PeCDD	ND< 0.0017	0.0015	0.0013	ND< 0.0017	ND< 2.1E-09	ND< 1.3E-06		
Total HxCDD	0.0028	0.0032	0.0029	0.0029	3.5E-09	2.2E-06	16%	0.0005
Total HpCDD	ND< 0.0028	0.0023	ND< 0.0021	ND< 0.0028	ND< 3.4E-09	ND< 2.1E-06		0.0005
Total TCDF	0.0056	0.0095	ND< 0.0016	0.0053	6.3E-09	4.1E-06		0.0108
Total PeCDF	0.0048	0.0026	0.0010	0.0028	3.3E-09	2.1E-06		0.0108
Total HxCDF	0.0030	0.0034	0.0034	0.0033	3.9E-09	2.5E-06	16%	0.0048
Total HpCDF	ND< 0.0020	ND< 0.0014	ND< 0.0014	ND< 0.0016	ND< 1.9E-09	ND< 1.2E-06	10%	
•				110 - 0.0010	ND ~ 1.9L-09	ND~ 1.2E-00		
Total PCDD	0.015	0.016	0.019	0.017	3.05.00	1.25.05		
Total PCDF	0.013	0.017		0.017	2.0E-08	1.3E-05	25%	0.004
			0.009	0.015	2.0E-08	1.2E-05	91%	0.014
Total PCDD/PCDF	0.035	0.033	0.028	0.032	4.0E-08	2.4E-05	30%	0.010

ND< - species not detected in sample.

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TABLE 4-25
AVERAGE PCDD/PCDF TOXIC EQUIVALENT DATA
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

		-		EPA Toxic				
Species		PCDF Emissions		Equivalent	EPA Toxic Equivalent, ng/Nm ³			
	ESP INLET	ESP OUTLET	STACK	Factors	ESP INLET	ESP OUTLET	STACK	
2378-TCDD	ND< 0.0020	0.0025	0.0023	1.0000	0.0020	0.0025	0.0023	
12378 PeCDD	0.0018	0.0017	ND< 0.0017	0.5000	0.0009	0.0023	0.0023	
123478 HxCDD	0.0049	0.0048	0.0042	0.1000	0.0005	0.0005	0.0004	
123678 HxCDD	ND< 0.0006	ND< 0.0007	ND< 0.0008	0.1000	0.0003	0.0003	0.0004	
123789 HxCDD	ND< 0.0009	ND< 0.0010	ND< 0.0011	0.1000	0.0001	0.0001	0.0001	
1234678 HpCDD	0.0028	0.0012	ND< 0.0028	0.0100	0.00003	0.0001	0.0001	
OCDD	0.0122	0.0048	0.0086	0.0010	0.00001	0.00001	0.00003	
2378 TCDF	ND< 0.0024	ND< 0.0010	0.0028	0.1000	0.0002	0.0001	0.0003	
12378 PeCDF	0.0011	ND< 0.0010	ND< 0.0008	0.0500	0.0002	0.0001	0.0003	
23478 PeCDF	ND< 0.0014	ND< 0.0012	0.0013	0.5000	0.0007	0.0001	0.0007	
123478 HxCDF	ND< 0.0012	ND< 0.0044	ND< 0.0009	0.1000	0.0001	0.0004	0.0007	
123678 HxCDF	ND< 0.0007	ND< 0.0013	ND< 0.0005	0.1000	0.0001	0.0004	0.0001	
234678 HxCDF	ND< 0.0012	ND< 0.0011	ND< 0.0009	0.1000	0.0001	0.0001	0.0001	
123789 HxCDF	0.0039	ND< 0.0066	0.0042	0.1000	0.0004	0.0007	0.0001	
1234678 HpCDF	ND< 0.0026	ND< 0.0011	ND< 0.0014	0.0100	0.00003	0.00001	0.00001	
1234789 HpCDF	ND< 0.0017	ND< 0.0012	ND< 0.0018	0.0100	0.00002	0.00001	0.00001	
OCDF	0.0025	ND< 0.0015	0.0032	0.0010	0.000002	0.000001	0.000002	
Total PCDD Toxic E	Equivalent, ng/Nm	3			0.0036	0.0040	0.0038	
Total PCDF Toxic E	quivalent, ng/Nm3				0.0018	0.0021	0.0017	
Total Toxic Equivale					0.0013	0.0021		
(2,3,7,8 TCDD Equi					0.0033	0.0001	0.0055	
Total Toxic Equivale	ent (detected speci	es), ng/Nm³			0.0019	0.0038	0.0041	
Total Toxic Equivale	•							
•		pooles). Hg/14III			0.0034	0.0023	0.0014	
Total Toxic Equivale					5.8E-09	6.9E-09	6.5E-09	
Fotal Toxic Equivale	nt, lb/10'*Btu				4.0E-06	4.4E-06	4.2E-06	



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limit or notably above field blank values. No dioxin or furan isomers were detected at levels greater than twice the field blank.

4.7 VOLATILE ORGANICS (VOST)

VOST tests for benzene and toluene were conducted at the ESP outlet and stack locations. The results of these measurements are presented in the following tables:

Table 4-26: VOST Test Results -- ESP Outlet

Table 4-27: VOST Test Results -- Stack

Table 4-28: VOST Samples -- Calculation of Percent Breakthrough

Benzene concentrations measured at the ESP outlet averaged 2.3 ppb compared to 1.1 ppb at the stack. This difference across the FGD is not considered significant. Average toluene concentrations measured at the ESP outlet of 23 ppb were significantly higher than that of 7.2 ppb measured at the stack. It is not clear whether this difference is due to actual FGD removal or if it is just an artifact of measurement uncertanty.

The mean blank level ranged from 0.026-0.029 ug/tube pair for benzene and 0.061-0.075 ug/tube pair for toluene, which meant blank corrections ranging from 27-47% of the reported laboratory value for benzene and 6.5-25% for toluene. Condensate fraction levels were significant for stack toluene only and contributed 26% to total reported levels.

Breakthrough measurements show that the method criteria of less than 30% breakthrough from the first collection tube to the second was exceeded on all three runs for stack toluene. The impact of this is that reported stack toluene emissions may be understated if there was also breakthrough past the back-up tenax/charcoal tube. Toluene field, trip and lab blanks ranged from 0.022 to 0.19 ug. This large variation in toluene blank values suggests that high enough levels of contamination may have existed in the back-up tenax/charcoal resin to create artificial breakthrough. Overall, sample results are very low and appear valid given their levels.

Conclusions:

Benzene concentrations measured at the ESP outlet averaged 2.3 ppb compared to 1.1 ppb at the stack. This difference across the FGD is not considered significant. Average toluene concentrations measured at the ESP outlet of 23 ppb were significantly higher than those of 7.2 ppb measured at the stack. It is not clear whether this difference is due to actual FGD removal or if it is just an artifact of measurement uncertanty.



VOST TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP OUTLET
AUGUST 1996

Test No.	1A-1D-VOST-OUT	2B-2D-VOST-OUT	3A-3D-VOST-OUT	AVERAGE	Unce	rtainty
Date	8/12/96	8/12/96	8/13/96		@95%CI	
Pitot Flow Rate, dscfm	320,301	320,301	316,771			
Sample Volume, dscf	0.68	0.68	0.68			
Fuel Factor, dscf/10 ⁶ Btu	12,328	12,539	12,158			
O ₂ , %	4.55	4.70	4.73			
CO ₂ , %	14.83	14.68	14.79			
Benzene						(ppb)
ppb	3.5	2.1	1.2	2.2	500/	
ug/Nm³	15	8.6	5.0	2.3 9.4	59%	1.3
lb/hr	0.016	0.010	0.006	0.010		
lb/10 ¹² Btu	10	6.3	3.6	6.7		
Γol uene						
ppb	19	20	29	23	50%	11
ug/Nm ³	66	69	102	7 9		
lb/hr	0.073	0.077	0.112	0.088		
lb/10 ¹² Btu	47	51	72	56		

Notes:

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⁽¹⁾ Each reported test run is the average of four sets of VOST tube pairs with the exception of Test #2, in which Test 2A was not reportable due to low internal recoveries.

⁽²⁾ Front and back tube pairs were desorbed and analyzed as one combined sample except for Trap Pairs A in which the front and back tubes were analyzed separately.

⁽³⁾ Laboratory sample results were blank corrected if the blank corrected result was greater than 3x the standard deviation of the mean blank.

⁽⁴⁾ The mean blank was determined from two field blank, one trip blank and four lab blank trap pairs.

TABLE 4-27

VOST TEST RESULTS

NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- STACK

AUGUST 1996

Test No.	1A-1C-VOST-STK	2A-2D-VOST-STK	3A-3E-VOST-STK	AVERAGE	Lince	ertainty
Date	8/12/96	8/12/96	8/13/96	TTERMOL		5%CI
Pitot Flow Rate, dscfm	341,987	341,987	320,789			37001
Sample Volume, dscf	0.65	0.67	0.64			
Fuel Factor, dscf/10 ⁶ Btu	13,290	13,342	12,585			
O ₂ , %	5.73	5.68	5.28			
CO ₂ , %	13.72	13.81	14.38			
Benzene				· · · · · · · · · · · · ·		(ppb)
ppb	1.7	1.0	0.56	1.1	50%	0.54
ug/Nm ³	6.9	4.1	2.3	4.4	2070	0.54
lb/hr	0.008	0.005	0.003	0.005		
lb/10 ¹² Btu	5.4	3.2	1.7	3.4		
oluene .						
ppb	10	6.0	5.8	7.2	38%	2.8
ug/Nm ³	34	21	20	25	5570	2.0
lb/hr	0.041	0.025	0.023	0.029		
lb/10 ¹² Btu	26	16	15	19		

Notes:

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⁽¹⁾ Each reported test run is the average of four sets of VOST tube pairs with the exception of Test #2, in which Test 2A was not reportable due to low internal recoveries.

⁽²⁾ Front and back tube pairs were desorbed and analyzed as one combined sample except for Trap Pairs A in which the front and back tubes were analyzed separately.

⁽³⁾ Laboratory sample results were blank corrected if the blank corrected result was greater than 3x the standard deviation of the mean blank.

⁽⁴⁾ The mean blank was determined from two field blank, one trip blank and four lab blank trap pairs.

TABLE 4-28

VOST SAMPLES -- CALCULATION OF PERCENT BREAKTHROUGH
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test No.	1A-VO	ST	2A-VO	ST	3A-VOST		
Analyte	Total ug/tube pair	Break- through ⁽¹⁾	Total ug/tube pair	Break- through ⁽¹⁾	Total ug/tube pair	Break- through ⁽¹⁾	
ESP OUTLET							
Benzene	0.29	27%	NR	NR	0.029	NB	
Toluene	1.5	NB	NR	NR	4.5	NB	
STACK							
Benzene	0.046	NB	0.10	NB	0.067	NB	
Toluene	0.10	97%(2)	0.49	31%(2)	0.28	39%(2)	

NB - no breakthrough to Tenax/charcoal (back-up) tube, analyte was found to be less than 0.075 ug in Tenax/charcoal (back-up) tube.

NR - analytical results for this tube pair not reportable due to low internal standard recoveries.

Notes:

- (1) Breakthrough = ug in Tenax/charcoal (back-up) tube / Total ug per tube pair x 100%
- (2) Exceeds 30% breakthrough and 0.075 ug in Tenax/charcoal (back-up) tube

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4.8 FORMALDEHYDE

Table 4-29 presents the test results of the formaldehyde measurements taken at the ESP outlet and stack locations. Formaldehyde concentrations were low at the ESP outlet ranging from not-detected to 1.6 ppb for an average of 0.9 ppb. Stack formaldehyde emissions were 10 times higher than the ESP outlet at 9.2 ppb. No formaldehyde was detected in the reagent blank. A possible source for the additional formaldehyde found at the stack is the formic acid, which can have formaldehyde as an impurity, used by the FGD process.

The formaldehyde field blank at the ESP outlet contained 6.1 ppb while the stack field blank had 9.4 ppb. The reason why the ESP outlet field blank level of formaldehyde is almost 7 times higher than the samples is not clear. At the stack, formaldehyde samples and field blank levels were similar suggesting that reported stack formaldehyde emissions may not be completely representative of the source.

Overall, formaldehyde concentration levels in both the stack samples and field blanks are considered low.

Conclusions:

Stack formaldehyde emissions averaged 9.2 ppb which was 10 times higher than ESP outlet concentrations measured at 0.9 ppb. A possible source for the additional formaldehyde is the formic acid, which can have formaldehyde as an impurity, used by the FGD process. On the other hand, stack formaldehyde sample and field blank levels were similar.

4.9 SULFUR OXIDES

The results of the sulfur oxide tests performed at the ESP outlet and stack are presented on Table 4-30. Average ESP outlet SO₂ concentrations of 1550 ppm compare to average stack concentrations of 146 ppm resulting in an FGD SO₂ removal efficiency for these time periods of 90.6%. Although these SO₂ results are similar to those from EPA Method 29, they do not match exactly since the controlled condensate sampling period was only 1-hour. Plant SO₂ CEMS data for corresponding time periods agree with ESP outlet and stack SO₂ results from this sample train. The average SO₃ result for the ESP outlet was 5.8 ppm and for the stack 4.9 ppm for an FGD removal rate of 15%. SO₃ amounts to 0.3% of ESP outlet SO₂ levels and 3.3% of stack levels.



TABLE 4-29
FORMALDEHYDE TEST RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

	ESP OUTLET									
Test No.	1-FORM-OUT	2-FORM-OUT	3-FORM-OUT	FB-FORM-OUT	AVERAGE	Uncertainty				
Date	8/13/96	0/12/07	0400			@95%CI				
Pitot Flow Rate, dscfm		8/13/96	8/13/96	8/13/96						
Sample Volume, dscf	316,771 66.41	319,404	326,628	320.934						
Fuel Factor, dscf/10 ⁶ Bti		71.16	72.49	70.02						
O ₂ , %	•	11,615	11,983	11,846						
=	4.44	3.97	4.49	4.30						
CO ₂ , %	14.57	15.22	14.80							
H ₂ O, %	8.0	8.0	8.6							
Formaldehyde		•				(ppb)				
ppb	0.89	1.6	ND<0.4	6.1	0.91	196% 1.8				
ug/Nm ³	1.2	2.2	ND<0.5	1	1.2	190% 1.8				
lb/hr	0.0013	0.0024	ND<0.006		0.0014					
lb/10 ¹² Btu	0.83	1.5	ND<0.4	5.6	0.0014					
	0.03	1.5	140.4	3.0	0.83					
			STA	CK						
Test No.	1-FORM-STK	2-FORM-STK	3-FORM-STK	FB-FORM-STK	AVERAGE	Uncertainty				
.						@95%CI				
Date	8/13/96	8/13/96	8/13/96	8/13/96						
Pitot Flow Rate, dscfm	320,789	348,971	353,892	341,217						
Sample Volume, dscf	68.25	73.93	74.29	72.15						
Fuel Factor, dscf/106Btu	•	12.462	12,565	12,376						
O ₂ , %	4.66	5.12	5.25	5.01						
CO ₂ , %	14.38	14.19	14.11							
H ₂ O, %	14.5	14.4	14.1		•					
Formaldehyde						(ppb)				
ppb	9.5	8.8	9.1	9.4	9.2	10% 0.9				
ug/Nm³	13	12	12		12	10/0 0.9				
~	0.014	0.014	0.015		0.015					
lb/hr	U.U.4									
lb/hr lb/10 ¹² Btu	9.0	8.5	8.9	9.1	8.8					

Note:

No formaldehyde was detected in the reagent blank.



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TABLE 4-30 SO₂ AND SO₃ TEST RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **AUGUST 1996**

1-SO3-OUT 8/7/96 324,594 48.29 13.080 5.57 13.86 7.8 1529 1786 7422 4.98	2-SO3-OUT 8/8/96 334,221 50.55 13.054 5.48 13.59 9.0 1542 1790 7704 5.02	3-SO3-OUT 8/9/96 335,700 50.06 13,337 5.77 13.58 7.7 1565 1852 7855 5.20		1546 1809
324,594 48.29 13.080 5.57 13.86 7.8 1529 1786 7422 4.98	334,221 50.55 13.054 5.48 13.59 9.0 1542 1790 7704	335,700 50.06 13,337 5.77 13.58 7.7 1565 1852 7855		1546
48.29 13.080 5.57 13.86 7.8 1529 1786 7422 4.98	50.55 13.054 5.48 13.59 9.0 1542 1790 7704	50.06 13,337 5.77 13.58 7.7 1565 1852 7855		
13.080 5.57 13.86 7.8 1529 1786 7422 4.98	13.054 5.48 13.59 9.0 1542 1790 7704	13,337 5.77 13.58 7.7 1565 1852 7855		
5.57 13.86 7.8 1529 1786 7422 4.98	5.48 13.59 9.0 1542 1790 7704	5.77 13.58 7.7 1565 1852 7855		
13.86 7.8 1529 1786 7422 4.98	13.59 9.0 1542 1790 7704	13.58 7.7 1565 1852 7855		
7.8 1529 1786 7422 4.98	1542 1790 7704	7.7 1565 1852 7855		
1529 1786 7422 4.98	1542 1790 7704	1565 1852 7855		
1786 7422 4.98	1790 7704	1852 7855		
1786 7422 4.98	1790 7704	1852 7855		
7422 4.98 6.6	7704	7855		1809
4.98 6.6				
6.6	5.02	5.20		7660
				5.07
	4.8	5.9		5.8
7.7	5.6	7.0		6.8
32	24	30		29
0.022	0.016	0.020		0.019
		STACK		-
1-SO3-STK	2B-SO3-STK		3B-SO3-STK	AVERAGE
8/7/96	8/8/96	8/9/96	8/9/96	ZieleE
333,778	329,113	334,012	331,223	
35.33	36.90	36.76	36.23	
13.037	12,986	13,302	13,372	
5.52	5.40	5.73	5.81	
13.91	13.42	13.62	13.66	
14.5	16.6	14.3	14.7	
129	202	141	113	146
150	233	166	134	171
645	995	703		725
0.420	0.654	0.467	0.376	0.479
91.6%	87.0%	91.0%	92.8%	90.6%
5.1	4.7	4.6	5.2	4.9
				4.9 5.7
				24
0.017				0.016
	#1.7 / U	· · ·		JAR.
		10	- WHM	DATE &
	0.022 1-SO3-STK 8/7/96 333,778 35.33 13.037 5.52 13.91 14.5 129 150 645 0.420 91.6% 5.1 6.0 26	0.022 0.016 1-SO3-STK 2B-SO3-STK 8/7/96 8/8/96 333,778 329,113 35.33 36.90 13.037 12,986 5.52 5.40 13.91 13.42 14.5 16.6 129 202 150 233 645 995 0.420 0.654 91.6% 87.0% 5.1 4.7 6.0 5.4 26 23 0.017 0.015	STACK STACK 1-SO3-STK 2B-SO3-STK 3A-SO3-STK 8/7/96 8/8/96 8/9/96 333,778 329,113 334,012 35.33 36.90 36.76 13.037 12.986 13,302 5.52 5.40 5.73 13.91 13.42 13.62 14.5 16.6 14.3 129 202 141 150 233 166 645 995 703 0.420 0.654 0.467 91.6% 87.0% 91.0% 5.1 4.7 4.6 6.0 5.4 5.4 26 23 23 0.017 0.015 0.015	STACK 1-SO3-STK 2B-SO3-STK 3A-SO3-STK 3B-SO3-STK 8/7/96 8/8/96 8/9/96 331,223 35.33 36.90 36.76 36.23 13,372 5.81 13.91 13.42 13.62 13.66 13.66 14.5 16.6 14.3 14.7 14.7 150 233 166 134 645 995 703 558 0.420 0.654 0.467 0.376 91.6% 87.0% 91.0% 92.8% 5.1 4.7 4.6 5.4 6.0 5.4 5.4 6.1 26 <t< td=""></t<>

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Conclusions:

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ESP outlet SO_3 levels were 5.8 ppm compared to 4.9 ppm at the stack. Average SO_2 results from the SO_3 sample train compare well with those from EPA Method 29 and plant CEMS data for corresponding time periods. ESP outlet SO_2 concentrations of 1550 ppm drop to 146 ppm at the stack for an FGD removal efficiency of 90.6%.

4.10 PARTICLE SIZE DISTRIBUTION

Particle size distribution results for the ESP outlet are given on Table 4-31. Particle size results for Tests 1 and 2 are in excellent agreement showing 82% of particulate less than less than 10 microns, 61% less than 2.5 microns, and 40% less than 1 micron in size. For Test 3, a more coarse particulate is reported with only 64% less than 10 microns, 48% less than 2.5 microns, and 28% less than 1 micron. The reasons for this difference between particle size distribution replicates is not clear but may be due to the limited single port sample grid used for testing. Tests 1 and 3 were performed in the North duct and Test 2 was performed in the South duct. The average cascade impactor total particulate concentration level of 0.0026 gr/dscf agrees reasonably well with the EPA Method 5 result of 0.0040 gr/dscf considering the significant differences between the traverse patterns and sample times used for each test method.

Conclusions:

Particle size distribution for the ESP outlet averaged 76% less than 10 microns, 56% less than 2.5 microns, and 36% less than 1 micron.

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TABLE 4-31
PARTICLE SIZE DISTRIBUTION RESULTS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM -- ESP OUTLET
AUGUST 1996

Size Cut Range,		A	verage Stag	e Emissic	$ms^{(1)}$			
Microns	1-PSD-OUT	2-PSD-OUT	3-PSD-OUT	Average	gr/dscf	mg/Nm ³	lb/hr	lb/MMBtu
	P	ercent Gained	in Size Cut Ran	ge				io/iviiviibtu
> 10.7	18.3	17.5	36.2	24.0	0.00086	2.11		
4.3 - 10.7	11.2	9.9	7.1	9.4	11	2.11	2.5	0.0016
2.1 - 4.3	13.5	13.2	10.5		0.00038	0.93	1.09	0.0007
1.2 - 2.1	17.1	19.6	17.9	12.4	0.00051	1.24	1.46	0.0009
0.59 - 1.2	17.7	17.5		18.2	0.00075	1.84	2.16	0.0014
0.30 - 0.59	14.7	17.5	13.1	16.1	0.00066	1.63	1.91	0.0012
< 0.30		_	9.0	12.1	0.00049	1.20	1.40	0.0009
· 0.50	<u>7.6</u>	<u> 2.6</u>	<u>6.1</u>	<u>7.8</u>	0.00034	<u>0.83</u>	0.98	0.0006
TOTALS	100.0	100.0	100.0	100.0	0.0040	9.8	11.5	0.0074
% < 10 microns	82	82	64	76	į			
% < 2.5 microns	59	62	48	56	1			
% < 1 micron	40	40	28	36				
Cascade Impactor,								
Gr/dscf:	0.0034	0.0021	0.0023	0.0026	H			
PA M5 Total PM,		0.0021	0.0023	U.UU20				
Gr/dscf:	0.0021	0.0074	0.0025	0.0040	ľ			
			***************************************	0.0070	II.			

Note: (1) Calculated from EPA Method 5 Total Particulate results and average % PSD values.

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SECTION 5.0

BOILER/ESP, FGD, AND WASTEWATER STREAMS SAMPLE RESULTS

This section is divided into three subsections: Unit 2 boiler/ESP solid stream sample results, FGD solid and liquid/sludge stream sample results, and wastewater treatment plant sample stream results. A mass balance for target inorganic elements is presented separately for the boiler/ESP and FGD process boundaries in their respective sections. For the wastewater treatment plant results, WWTP removal efficiencies of target elements are provided. Comparisons between baseline and post-retrofit test program solid stream sample results are not discussed in this section (see Section 7.0).

5.1 BOILER/ESP SOLID STREAM SAMPLE RESULTS

This subsection begins with an overview of the calculation procedures used for solid stream process flow rates. Sample results for coal, bottom ash, and flyash are discussed individually, and then combined with ESP inlet and ESP outlet flue gas measurements to construct the boiler/ESP mass balance.

Solid Process Stream Flow Rates and Ash Mass Balance

To understand the material balance results presented in Section 5.1.5, an explanation of the calculation procedures used to determine inorganic solid stream results is important. Please refer to Section 2.2.2 for explanations on how raw solid stream flow rate measurements were made.

Table 5-1 presents a comprehensive step-by-step review of the calculations used for obtaining stream flow rates on a lb/10⁶Btu basis. Stream flow rate calculations on a lb/hr basis can be found in Appendix C.21. The stream flow rates are combined with reported sample analyte concentration levels in mg/kg (or ppm by weight) to obtain analyte solid stream results using the following equations:

Analyte Emission Factor, $lb_{(analyte)}/10^{12}Btu_{(fuel\ input)} = Analyte Concentration,$ 1) mg_(analyte)/kg_(solid stream) * Solid Stream Flow Rate, lb_(solid stream)/10⁶Btu_(fuel input)

Coal Flow Rate_(as det. or dry), lb/10⁶Btu = 10⁶/Coal Flow Rate_(as det. or dry), lb/10⁶Btu = 10⁶/Coal Flow Rate_(as det. or dry) la)

TABLE 5-1 ASH FLOW RATE WORKSHEET NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM AUGUST 1996

Parameter		FLOW RA	ATE, Ib/10° Btu		Average
	Test 1	Test 2	Test 3	Average	RPDM
Coal Flow Rate (as det.), lb/hr(1)	110,322	114,454	115,115	113,297	1.0%
Coal HHV (as det.), Btu/ib	13.612	13,648	13,522	13,594	0.4%
Coal Flow Rate, as det. (2)	73.46	73.27	73.96	73.56	0.4%
Coal HHV (dry), Btu/lb	13,731	13,791	13.661	13.728	0.3%
% Ash in Fuel, dry	9.41%	9.01%	9.69%	9.37%	2.6%
Total Ash Input ⁽³⁾	6.85	6,53	7.09	6.83	2.9%
Calculated Flyash Flow Rate (From EPA	Method 5 Results):				
ESP Inlet M5 Flow Rate, as det.	5.40	6.32	7.35	6.35	10.4%
ESP Outlet M5 Flow Rate, as det.	0.004	0.014	0.004	0.007	58.6%
Flyash Flow Rate, as det.	5.39	6.30	7.34	6.35	10.5%
ESP Inlet Flyash Ash, %	96.88%	97.19%	97.29%	97.12%	0.2%
ESP Inlet Flyash As Det. H ₂ 0, %	0.14%	0.05%	0.07%	0.09%	41.0%
Flyash Flow Rate (Ash Only), dry	5.22	6.12	7.14	6.16	10.6%
Calculated Flyash Flow Rate (From EPA	Method 29 Results):				
ESP Inlet M29 Flow Rate, as det.	6.23	7.15	7.40	6.93	6.8%
ESP Outlet M5 Flow Rate, as det.	0.004	0.014	0.004	0.007	58.6%
Flyash Flow Rate, as det.	6.22	7.14	7.40	6.92	6.7%
ESP Inlet Flyash Ash, %	96.88%	97.19%	97.29%	97.12%	0.2%
ESP Inlet Flyash As Det. H ₂ 0, %	0.14%	0.05%	0.07%	0.09%	41.0%
Fiyash Flow Rate (Ash Only), dry	6.02	6.94	7.19	6.71	6.9%
Measured Botttom Ash Flowrate:					
Bottom Ash Rate (as rec'd), lb/hr	1,565	1,693	1,877	1,712	6.5%
Bottom Ash Total H ₂ 0, %	22.29%	23.84%	22.19%	22.77%	3.1%
Bottom Ash As Det. H ₂ 0, %	0.22%	0.03%	0.06%	0.10%	75.3%
Bottom Ash Rate (as Jet.), lb/hr	1,219	1,289	1,461	1.323	7.0%
Bottom Ash Flow Rate, as det. (4)	0.812	0.825	0.939	0.859	6.2%
Bottom Ash Ash, % (dry)	98.60%	99.05%	99.45%	99.03%	0.3%
Bottom Ash Rate (Ash Only), dry	0.798	0.817	0.933	0.850	6.6%
Ash Only Mass Balance (Output/Input): (5)				
Using EPA M5 Flyash Flow Rate	87.8%	106.4%	113.9%	102.8%	9.6%
Using EPA M29 Flyash Flow Rate	99.5%	118.9%	- 114.6%	110.9%	6.9%
EPA M29 Ash Correction Factor ⁽⁶⁾	1.005	0.822	0.856		

All calculations are based on ASTM D3180.

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⁽¹⁾ Fuel flow rate calculated from measured ESP Outlet Method 29 pitot flow rates and F-factor using EPA Method 19. See Table 5-2A.

⁽²⁾ Coal Flow Rate (as det.), lb/MMBtu = 106/Coal HHV. Btu/lb (as det.)

⁽³⁾ Total Ash Input, lb/MMBtu = Coal Flow Rate, lb/MMBtu (dry) * Fuel Ash, wt.% / 100 (dry)

⁽⁴⁾ Bottom Ash Flow Rate, ib(ash)/MMBtu = ib(ash)/hr, as det. / ib(fuel)/hr, as det. / HHV. Btu/lb as det. * 106

⁽⁵⁾ Mass Balance (Output/Input) = (ESP Outlet Ash Only, lb/MMBtu + Flyash Ash Only, lb/MMBtu + Bottom Ash Ash Only, lb/MMBtu) / Total Ash Input, lb/MMBtu

⁽⁶⁾ Ash correction factor calculated from EPA M29 ash mass balance results was used to normalize EPA M29 solids catches to 100% ash balance.

- Ash Flow Rate_(as det. or dry), $lb/10^6$ Btu = $lb_{(ash, as det. or dry)}/hr * <math>1/lb_{(fuel, as det or dry)}/hr$ 1b) * 1/HHV_(as det. or dry) * 10⁶
- Analyte Mass Emission, lb_(analyte)/hr = Analyte Concentration, mg_(analyte)/kg_(solid stream) 2) * Solid Stream Flow Rate, lb_(solid stream)/hr * 10⁻⁶

As discussed in Section 2.2.2.1, the coal firing rate was back-calculated from pitot measurements of the ESP outlet flue gas flow rates using an EPA Method 19 F-factor. These calculations for obtaining coal feed rates on a lb/hr basis are presented for the inorganic test period (i.e. mass balance test period) on Table 5-2A, and for the organic test period on Table 5-2B. Flyash flow rates were obtain from the difference between measured ESP inlet and ESP outlet particulate concentrations from both EPA Method 5 and Method 29 sample trains. Flyash flow rates as determined from the Method 5 results were used for subsequent mass balance calculations.

The weight basis for the solid stream flow rates are presented on an as-determined basis (i.e. the sample weight includes as-determined or residual moisture levels), dry basis (no moisture in the sample), or an "ash-only," dry basis (dry weight excluding carbon, sulfur, etc) depending on the basis for which the analyte results are reported by the laboratory. For trace metals, solid stream flow rates were converted to an as-determined basis. For major elements, coal rates on a dry (whole coal) basis and ash rates on an ash-only, dry basis were needed. All solid stream flow rates were converted to an "ash only" basis to determine an ash mass balance. As shown on Table 5-1 the average ash balance using EPA Method 5 flyash flow rates was excellent, but exhibited notable variability, averaging 102.8%.

The ash balance calculated from EPA Method 29 flyash results indicate that the Method 29 ESP inlet particulate levels are overstated for Tests 2 and 3 by 15-20%. A closer examination reveals that a disproportionately high amount of solids were collected in the front-halves of these sample trains. Assuming that the ash balance provides a bench mark for ash distribution levels across the boiler/ESP process streams, Tests 2 and 3, which collected 36.6 and 33.7 grams of proberinse solids, respectively, collected 5-7 grams too much. To eliminate this potential 15-20% bias in ESP inlet trace and major element concentration levels, the total solids catch amounts for Runs 2 and 3 were adjusted based on ash balance data before multiplying them by target element concentration values reported by the laboratory.

A significant measurement bias on the order of 15-25% was associated with the May 1994 baseline ESP inlet particulate results based on their ash mass balance. It was postulated that the highly irregular dimensions of the ESP iniet unce, containing the sample location, creates non-axial flow conditions which can succeed just prior to the sample location, creates non-axial flow conditions which can succeed the concentrations of particulate. Flyash stratification can introduce both positive and negative biases

TABLE 5-2A
FUEL FLOW RATE CALCULATIONS -- INORGANIC TEST PERIOD
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

	_	Inorganic Test Pe	eriod
Parameter	Test 1	Test 2	Test 3
ESP Inlet M5 Pitot Flow Rate, dscfm	319,669 *	344,157	220.496
ESP Inlet M29 Pitot Flow Rate, dscfm	325,318 *	340,247 *	329,486 327,659
ESP Outlet M5 Pitot Flow Rate, dscfm	325,833	336,795	341,319
ESP Outlet M29 Pitot Flow Rate, dscfm ⁽¹⁾	323,354	331,647	330,081
F-Factor, dscf/MMBtu @ 0% O ₂	9594	9631	9655
HHV, Btu/lb (dry)	13,731	13,791	13,661
ESP Outlet M29 Flue Gas O ₂ ,%	5.38	5.10	5.04
Fuel Flow, lb/hr (dry) ⁽²⁾	109,368	113,264	113,940
Fuel Total Moisture, %	4.81	5.77	5.93
Fuel Flow, lb/hr (as-rec'd)	114,895	120,199	121,123
Fuel As-Determined Moisture, %	0.86	1.04	1.02
Fuel Flow, lb/hr (as-det.)	110,322	114,454	115,115
Boiler Efficiency, Btu/kW-hr	9745	9745	9745
Jnit 2 Load, MW (gross)	158.60	159.38	158.81
ESP Outlet Location:			
Calculated Heat Rate Flow Rate, dscfm ⁽³⁾	332,789	329,765	328,186
ercent Diff. from ESP Outlet M29 flow rate	-2.84%	0.57%	0.58%

^{*}Differences between measured pitot flow rates and calculated heat rate flow rates > 3%. See Table 4-3 for comparisons.

Notes

- (1) ESP Outlet M29 flow rates chosen to calculated fuel flow since all differences were less than 3%.
- (2) Fuel Flow, lb/hr (dry) = Pitot Flow Rate, dscfm / F-Factor, dscf/MMBtu / 20.9 * (20.9 Flue Gas O_2 ,%) / HHV, Btu/lb * 10^6 * 60 min/hr
- (3) Calculated Heat Rate Flow Rate, dscfm = Boiler Eff., Btu/kW-hr * Unit 2 Load, MW (gross)
- * 1000 * F-Factor, dscf/MMBtu / 10^6 * 20.9/(20.9-Flue Gas, O₂%) / 60 min/hr

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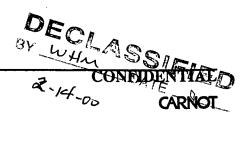
TABLE 5-2B
FUEL FLOW RATE CALCULATIONS -- ORGANIC TEST PERIOD
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

	(Organic Test Per	iod
Parameter	Test 1	Test 2	Test 3
ESP Inlet M23 Pitot Flow Rate, dscfm	313,044 *	319,429 *	311,472
ESP Outlet M23 Pitot Flow Rate, dscfm ⁽¹⁾	321,952	320,301	321,047
F-Factor, dscf/MMBtu @ 0% O ₂	9644	9719	9409
HHV, Btu/lb (dry)	13,657	13,511	13,752
ESP Outlet M23 Flue Gas O ₂ ,%	4.40	4.96	4.22
Fuel Flow, lb/hr (dry) ⁽²⁾	115,790	111,620	118,807
Fuel Moisture, %	5.57	7.26	6.96
Fuel Flow, lb/hr (as-rec'd)	122,620	120,358	127,694
Boiler Efficiency, Btu/kW-hr	9745	9745	9745
Unit 2 Load, MW (gross)	157.53	156.57	158.84
ESP Outlet Location:			
Calculated Heat Rate Flow Rate, dscfm ⁽³⁾	312,542	324,056	304,161
Percent Diff. from ESP Outlet M23 flow rate	3.01%	-1.16%	5.55%

^{*}Differences between measured pitot flow rates and calculated heat rate flow rates > 6%. See Table 4-4 for comparisons.

Notes:

- (1) ESP Outlet M23 flow rates chosen to calculated fuel flow since all differences were less than 6%.
- (2) Fuel Flow, lb/hr (dry) = Pitot Flow Rate, dscfm / F-Factor, dscf/MMBtu / 20.9 * (20.9 Flue Gas O_2 ,%) / HHV, Btu/lb * 10^6 * 60 min/hr
- (3) Calculated Heat Rate Flow Rate, dscfm = Boiler Eff., Btu/kW-hr * Unit 2 Load, MW (gross)
- * 1000 * F-Factor, dscf/MMBtu / 10^6 * 20.9/(20.9-Flue Gas, O₂%) / 60 min/hr



in any particulate measurements made at the ESP inlet, and can potentially cause a high degree of variability or even overstatement of results obtained by Method 5 and 29 to occur.

Ash distribution across the boiler/ESP output streams normalized to 100% shows 87.8% of total ash exits the system as ESP flyash, 12.1% leaves as bottom ash, and 0.1% continues onto the FGD in the flue gas.

5.1.2 Coal Feed

Coal samples collected during the inorganic test period were analyzed for ultimate parameters, higher heating value, ash, moisture, and trace and major elements including anion precursors. Coal samples obtained during the organic test period were only analyzed for ultimate and higher heating value.

5.1.2.1 Ultimate Analysis

Ultimate parameters, ash, moisture, heating value, and EPA Method 19 F-factors are presented on Table 5-3 for the inorganic (Tests 1-3) and organic (Tests 4-6) test period coals. Daily F-factors were used in all corresponding lb/10¹²Btu flue gas emission factor calculations as shown in Appendix D. As mentioned in Section 2.2.2.1 the coal fired during this test program was a 50/50 blend of raw and pre-cleaned coal. As such, a larger variability is expected between daily coal sample results than if the coal was 100% pre-cleaned. The results of the ultimate analyses (excluding chlorine) of the inorganic test period coal exhibit good agreement (95% CI < 15%) between daily samples. For the organic test period coal, higher variability is seen for reported ash and oxygen levels. The smaller number of sampling increments taken and the 50/50 coal blend may be contributing factors; however, 4-COAL and 5-COAL are splits of the same gross sample obtained on 8/12/96, and there still was a 9% difference between reported ash levels suggesting that at least some of the variability is analytical in nature.

5.1.2.2 Trace Elements

Results of the trace element and anion precursor analyses of the three inorganic coals are presented on Table 5-4. All target trace elements were detected in the coal samples. Excellent agreement (95% CI < 25%) between test replicates can be seen for most trace elements. For molybdenum, 3-COAL was not included in the average, so a higher uncertainty level was obtained since only two valid replicates requires a higher t-value. The reported molybdenum concentration of 3-COAL does not agree with other boiler/ESP process stream levels and is considered an outlier. For the group of trace elements reported, phosphorus and barium are the predominant elements found in the coal.

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TABLE 5-3 COAL ULTIMATE/PROXIMATE ANALYSIS REPORT NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **AUGUST 1996**

Test Number	1-COAL	2-COAL	3-COAL	Average	95% CI	4-COAL	5-COAL	6-COAL	Average	95% CI
Sample Date	8/7/96	8/8/96	8/9/96			8/12/96	8/12/96	8/13/96	Avciage	93 /6 CI
Sampe Time	815/1545	805/1545	805/1545			910/1900		910/1530		
Ultimate/Proximate Analysis	s (Drv Bas	is):								·
%Carbon	75.83	75.81	75.48	75.71	0.6%	75.58	75.03	74.35	74.99	2.00/
%Hydrogen	4.63	4.94	4.84	4.80	8.2%	4.74	4.78	4.87	4.80	2.0%
%Nitrogen	1.49	1.47	1.59	1.52	10.5%	1.41	1.54	1.43		3.4%
%Sulfur	2.51	2.55	2.33	2.46	11.8%	2.41	2.45	2.36	1.46 2.41	11.9%
%Ash (@550°C)	9.41	9.01	9.69	9.37	9.1%	9.76				4.7%
%Oxygen (by difference)	6.05	6.12	5.98	6.05	2.9%		10.68	9.00	9.81	21.3%
%Chlorine	0.03	0.12	0.09	0.03		5.99	5.42	7.89	6.43	49.9%
	0.00	0.10	0.09	0.09	27.6%	0.11	0.10	0.10	0.10	14.4%
Total Moisture, %	4.81	5.77	5.93	5.50	27.3%	5.57	7.26	6.96	6.60	33.9%
Air Dry Loss, %	3.98	4.78	4.96	4.57	28.3%	4.53	6.24	6.00	5.59	41.1%
As-Det./Residual Moisture, %	0.86	1.04	1.02	0.97	24.5%	1.09	1.09	1.02	1.07	9.1%
HHV, Btu/ib (dry)	13,731	13,791	13,661	13,728	1.2%	13,657	13,511	12.752	12.640	2.20/
HHV, Btu/lb (as det.)	13,612	13,648	13,522	13,726	1.2%			13,752	13,640	2.2%
HHV, Btu/lb (as rec'd)	13,071	12,995	12,851	•		13,508	13,364	13,612	13,495	2.3%
(13,071	14,373	12,031	12,972	2.1%	12,896	12,530	12,795	12,740	3.7%
F-Factor, dscf/MMBtu @0% O ₂	9,594	9,631	9,655	9,626	0.8%	9,644	9,719	9,409	9,589	4.2%

EPA Method 19 F-Factor Calculation @68°F:

F-Factor, dscf/MMBtu @0% $O_2 = 10^6$ [3.64(%H,dry)+1.53(%C,dry)+0.14(%N,dry)+0.57(%S,dry)-0.46(% O_2 ,dry (fuel))] / HHV,Btu/lb (dry)



TABLE 5-4
TRACE ELEMENT BITUMINOUS COAL ANALYSIS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-COAL	2-COAL	3-COAL		AVERAGE	3	Unce	ertainty
Date	8/7/96	8/8/96	8/9/96				@9	5%CI
Fuel Flow, lb/hr (as det.)	110,322	114,454	115,115					
HHV, Btu/lb (as det.)	13,612	13,648	13,522					
Total Moisture, %	4.81	5.77	5.93					
As Det. Moisture, %	0.86	1.04	1.02					
Element	mg/kg	mg/kg	mg/kg	mg/kg	lb/hr	lb/10 ¹² Btu	%	mg/kg
	Who	ole Coal (As-I	Determined B	asis)				
Trace Elements								
Antimony	0.31	0.30	0.33	0.31	0.036	23	12%	0.04
Arsenic	6.9	7.6	6.5	7.0	0.79	515	20%	1.38
Barium	76.0	74.9	76.6	75.8	8.6	5,579	3%	2.1
Beryllium	0.80	0.87	0.79	0.82	0.093	60	13%	0.11
Cadmium	0.040	0.042	0.050	0.044	0.005	3.2	30%	0.01
Chromium	11	11	11	11	1.2	809	0%	0.0
Cobalt	2.7	2.5	2.6	2.6	0.29	191	10%	0.25
Copper	7.5	7.2	7.0	7.2	0.82	532	9%	0.62
Lead	3.69	3.81	4.21	3.90	0.44	287	17%	0.68
Manganese	18.1	21.7	18.9	19.6	2.2	1,439	24%	4.7
Mercury	0.100	0.106	0.096	0.101	0.011	7.4	12%	0.01
Molybdenum ⁽¹⁾	1.6	1.4	2.9	1.5	0.17	110	85%	1.3
Nickel	8.09	7.99	8.15	8.08	0.92	594	2%	0.20
Phosphorus	218	236	258	237	27	17,280	21%	50
Selenium	1.2	1.3	1.1	1.2	0.14	88	21%	0.25
Vanadium	16	17	16	16	1.9	1,201	9%	1.4
Anion Precursors, (Dry Ba	sis)							
Chlorine	840	955	850	882	99	64,238	18%	158
Fluorine	92	_ 99	98	96	10.8	7,005	11%	10.1
Sulfur	25,100	25,500	23,300	24,633	2,763	1.79E+06	12%	2,909

Note: (1) Molybdenum value for 3-COAL was not included in the average, result appears biased high and does not agree with other process stream levels.



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5.1.2.3 Anion Precursors

Significant levels of chlorine and fluorine were found in the coal. Chlorine and sulfur results are from the ultimate analyses presented on Table 5-3 converted to a ppm basis. Excellent agreement between anion precursor replicate results can be seen.

5.1.2.4 **Major Elements**

Table 5-5 provides the major ash element concentrations of the coal samples on a dry, whole coal basis. Excellent agreement can be seen between test replicates for all ash elements. Silicon, iron, and aluminum were the predominant elements detected. Emission factor results are given in units of lb/106Btu.

5.1.3 Bottom Ash

Table 5-6 reports the ultimate analyses results for both the bottom ash and flyash. The carbon content of the bottom ash was found to be 0.70% by weight on average.

Trace element and anion precursor results for the bottom ash are given on Table 5-7. Only antimony and selenium were reported below the analytical detection limit. Consistent with the coal, phosphorus and barium were the predominant trace elements detected. Excellent agreement between bottom ash replicates can be seen for most trace elements and anion precursors. Good agreement (uncertainties between 25-50%) is shown for arsenic sample values. Higher variability in mercury and sulfur bottom ash results is not considered significant since their levels amount to only 0.1% of their coal input level.

Table 5-8 presents the major ash element concentrations in the bottom ash on a percent basis. Silicon, iron, and aluminum are the predominant elements as expected. Agreement among test replicates was excellent for most major elements and good for sodium. Emission factor results are given in units of lb/106Btu to correspond with the coal.

5.1.4 Flyash

As shown on Table 5-6, flyash carbon levels averaged 2.2%.

Trace element and anion precursor analyses of the flyash are reported on Table 5-9 and show all target parameters were detected. Excluding sulfur, flyash phosphorus and barium were the predominant elements similar to the coal and bottom ash. Excellent agreement among replicates is shown for most elements, while good agreement can be seen for mercury. Fluorine concentrations in the flyash exhibited poor agreement; however flyorine flyash levels are only 2.4% of coal input.

TABLE 5-5 MAJOR ASH ELEMENTS BITUMINOUS COAL ANALYSIS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **AUGUST 1996**

Test Number	1-COAL	2-COAL	3-COAL		AVERAG	E	Unc	ertainty
Date	8/7/96	8/8/96	8/9/96					95%CI
Fuel Flow, lb/hr (dry)	109,368	113,264	113,940					30.001
HHV, Btu/lb (dry)	13,731	13,791	13,661					
Fuel Ash, % (dry)	9.41	9.01	9.69					
Fuel Moisture, %	4.81	5.77	5.93					
Element	mg/kg	mg/kg	mg/kg	mg/kg	lb/hr	lb/10 ⁶ Btu	%	mg/kg
		Whole Coal	(Dry Basis)					
Major Elements								
Aluminum	10,498	9,856	10,913	10,423	1169	0.759	13%	1,322
Calcium	3,504	3,844	3,996	3,781	425	0.275	17%	626
Iron	12,867	13,013	11,942	12,607	1414	0.918	11%	1,442
Magnesium	489	494	527	503	56	0.037	10%	51
Phosphorus	218	236	258	237	27	0.017	21%	50
Potassium	1,281	1,212	1,359	1,284	144	0.094	14%	184
Silicon	19,683	17,916	20,663	19,421	2179	1.42	18%	3,456
Sodium	532	520	548	533	60	0.039	7%	35
Titanium	525	475	534	511	57	0.037	15%	79



TABLE 5-6 BOTTOM ASH & FLYASH ULTIMATE ANALYSIS REPORT NYSEG POST-RETROFIT TEST PROGRAM **AUGUST 1996**

Test Number	1-BottomAsh	2-BottomAsh	3-BottomAsh	Average	I-Flyash	2-Flyash	3-Flyash	Average
Sample Date	8/7/96	8/8/96	8/9/96	_	8/7/96	8/8/96	8/9/96	
Sampe Time	1800	1830	1645		910/1610	909/1620	919/1500	
Ultimate Analysis (Dry B	asis):							
%Carbon	1.19	0.67	0.25	0.70	2.43	2.17	2.04	2.21
%Hydrogen	0.07	0.03	0.05	0.05	0.09	0.05	0.02	0.05
%Nitrogen	0.01	0.01	0.01	0.01	0.10	0.02	0.01	0.03
%Sulfur	0.04	0.07	0.20	0.10	0.48	0.45	0.42	0.04
%Ash (@550°C)	98.60	99.05	99.45	99.03	96.88	97.19	97.29	97.12
%Oxygen (by difference)	0.08	0.16	0.03	0.09	0.01	0.11	0.21	
%Chlorine	0.01	0.01	0.01	0.01	0.01	0.01	0.21	0.11 0.01
Total Moisture, %	22.29	23.84	22.19	22.77	0.32	0.05	0.62	0.22
Air Dry Loss, %	22.12	23.82	22.14	22.69	0.18	0.00		0.33
As-Det./Residual Moisture,	0.22	0.03	0.06	0.10	0.14	0.05	0.55 0.07	0.24 0.09



TABLE 5-7
TRACE ELEMENT BOTTOM ASH ANALYSIS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-BottomAsh	2-BottomAsh	3-BottomAsh		AVERAGE		Unc	ertainty
Date	8/7/96	8/8/96	8/9/96					95%CI
As-Determined Basis:								/3/0C1
Bottom Ash Flow, lb/hr	1,219	1,289	1,461					
Bottom Ash, lb/106Btu	0.81	0.83	0.94					
Total Moisture, %	22.29	23.84	22.19					
As Det. Moisture, %	0.22	0.03	0.06					
Element	mg/kg	mg/kg	mg/kg	mg/kg	lb/hr	lb/10 ¹² Btu	%	mg/kg
		As-Determi				ib/10 Btu	70	mg/ wg
Trace Metals								
Antimony	ND<1	ND<1	ND<1	ND<1	ND<0.001	ND<0.86		
Arsenic	7.6	9.56	9.85	9.0	0.012	7.8	34%	
Barium	671	657	662	663	0.88	7.8 569		3.0
Beryllium	6.04	5.75	5.57	5.79	0.008	5.0	3%	18
Cadmium	0.069	0.082	0.078	0.076	1.0E-04		10%	0.59
Chromium	110	100	103	104	0.138	0.066 90	22%	0.01
Cobalt	29.4	28.6	28.8	28.9	0.138		12%	13
Copper	64	63	60	62	0.038	25 53	4%	1.0
Lead	10.7	11.9	12.8	11.8	0.082	53	8%	5
Manganese	236	234	234	235	0.016	10	22%	2.6
Mercury	0.014	0.021	ND<0.01	0.013	0.31 1.7E-05	201	1%	3
Molybdenum	6.8	6.6	7.0	6.80	0.009	0.011	149%	0.020
Nickel	106	103	98.8	103	0.009	5.8	7%	0.50
Phosphorus	2,095	2,269	2,400	2,255	3.0	88	9%	9
Selenium	ND<0.6	ND<0.6	2,400 ND<0.6	ND<0.6	3.0 ND<0.001	1,923	17%	380
Vanadium	140	139	141	140		ND<0.52		
	110	137	141	140	0.19	120	2%	2
nion Precursors, (Dry 1	Basis) -							
Chlorine	129	131	129	130	0.17	111	3%	4
Fluorine	26	26	26	26	0.034	22	3%	1
Sulfur	386	657	2056	1033	1.44	928	215%	2226



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TABLE 5-8
MAJOR ASH ELEMENT BOTTOM ASH ANALYSIS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-BottomAsh	2-BottomAsh	3-BottomAsh		AVERAG	E	Une	certainty
Date	8/7/96	8/8/96	8/9/96					95%CI
Ash Only (Dry Basis):								
Bottom ash Flow, lb/hr	1,199	1,277	1,453					
Bottom Ash, lb/106Btu	0.798	0.817	0.933					
BottomAsh Ash, %	98.60	99.05	99.45					
BA Moisture, %	22.3	23.8	22.2					
Element	% Conc.	% Conc.	% Conc.	% Conc.	lb/hr	lb/10 ⁶ Btu	%	% Conc
Major Elements								
Aluminum	10.0	9.9	9.9	9.9	130	0.084	1%	0.1
Calcium	4.3	4.9	4.7	4.6	61	0.040	16%	0.8
Iron	20.8	19.2	18.0	19.3	252	0.16	18%	3.5
Magnesium	0.57	0.65	0.55	0.59	7.7	0.0050	20%	0.12
Phosphorus	0.21	0.23	0.24	0.23	3.0	0.0019	17%	0.04
Potassium	1.0	1.1	1.1	1.1	14	0.009	14%	0.1
Silicon	19.1	19.6	20.4	19.7	259	0.17	8%	1.5
Sodium	0.39	0.42	0.57	0.46	6.1	0.0040	52%	0.24
Titanium	0.46	0.47	0.48	0.47	6.2	0.0040	7%	0.03

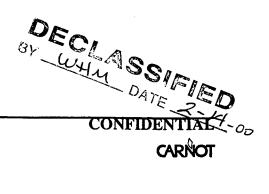


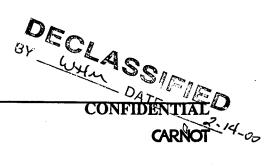
TABLE 5-9
TRACE ELEMENT FLYASH ANALYSIS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-FLYASH	2-FLYASH	3-FLYASH		AVERAGE		Une	ertainty
Date	8/7/96	8/8/96	8/9/96					95%CI
As-Determined Basis:								237 0C 1
Flyash Flow, lb/hr	7,861	9,937	10,905					
Flyash Flow, lb/10 ⁶ Btu	5.39	6.30	7.34					
Total Moisture, %	0.32	0.05	0.62					
As Det. Moisture, %	0.14	0.05	0.07					
Element	mg/kg	mg/kg	mg/kg	mg/kg	lb/hr	lb/10 ¹² Btu	%	mg/kg
		As-Determ	ined Basis				,,	me, ve
Trace Metals								
Antimony	3.2	3.1	3.1	3.1	0.030	20	5%	0.1
Arsenic	85	81.5	75.5	81	0.77	509	15%	12
Barium	816	777	779	7 91	7.5	5,005	7%	55
Beryllium	7.62	7.32	6.85	7.26	0.069	46	13%	0.96
Cadmium	0.41	0.39	0.38	0.39	0.004	2.5	10%	0.90
Chromium	119	115	114	116	1.1	734	6%	7
Cobalt	28.5	27.0	27.8	27.8	0.27	176	7%	1.9
Copper	69.7	68.6	68.0	68.8	0.66	436	3%	2.1
Lead	40	40.3	40.7	40	0.39	256	2%	1
Manganese	189	192	189	190	1.8	1,206	2%	4
Mercury	0.086	0.072	0.107	0.088	8.5E-04	0.57	50%	0.044
Molybdenum	16	16	16	16	0.15	102	0%	0.044
Nickel	75.7	73.4	73.3	74.1	0.71	470	5%	3.4
Phosphorus	2,837	2,531	2,749	2,706	25	16,640	14%	391
Selenium	2.8	3.1	2.9	2.9	0.028	19	13%	0.4
Vanadium	175	174	171	173	1.7	1,099	3%	5
nion Precursors, (Dry I	Basis)							
Chlorine	100	100	101	100	0.96	636		1
Fluorine	20	40	20	27	0.26	169	107%	29
Sulfur	4800	4500	4200	4500	43	28,336	17%	745



TABLE 5-10
MAJOR ASH ELEMENT FLYASH ANALYSIS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-FLYASH	2-FLYASH	3-FLYASH		AVERAG	Ē	Un	certainty
Date	8/7/96	8/8/96	8/9/96					95%CI
Ash Only (Dry Basis):	,							,557661
Flyash Flow, lb/hr	7,605	9.653	10.602					
Flyash Flow, lb/106Btu	5.22	6.12	7.14					
Flyash Ash, %	96.88	97.19	97.29					
Flyash Moisture, %	0.32	0.05	0.62					
Element	% Conc.	% Conc.	% Conc.	% Conc.	lb/hr	lb/10 ⁶ Btu	%	% Conc
		Ash Only (l	Dry Basis)					
<u> Major Elements</u>								
Aluminum	11.2	11.3	11.2	11.2	1044	0.692	2%	0.2
Calcium	4.1	4.2	4.0	4.1	379	0.251	5%	0.2
Iron	13.5	13.5	13.3	13.4	1246	0.827	2%	0.3
Magnesium	0.57	0.63	0.57	0.59	55	0.036	15%	0.09
Phosphorus	0.28	0.25	0.27	0.27	25	0.017	14%	0.04
Potassium	1.5	1.5	1.5	1.5	137	0.091	3%	0.04
Silicon	21.8	21.7	22.2	21.9	2036	1.350	3%	0.7
Sodium	0.61	0.56	0.50	0.56	51	0.034	23%	0.13
Titanium	0.56	0.56	0.55	0.56	52	0.034	3%	0.01



Similar to the bottom ash, flyash major elemental composition results presented on Table 5-10 are in units of %Concentration and lb/10⁶Btu. Silicon, iron, and aluminum combined make up 46.5% of the flyash on an elemental basis. Agreement between sample values was excellent.

5.1.5 Boiler/ESP Mass Balance

The purpose of performing a mass balance is to provide a quality assurance assessment of the flue gas and solid stream sample data. By examining the degree of closure for a particular element, in combination with historical analytical difficulties and associated uncertainty levels, questionable data points can be uncovered and investigated. Statements regarding the magnitude and direction (both positive and negative) of any bias associated with the measurement of that data point can then be made. EPRI and DOE consider material balance closures between 70-130% for trace elements and anion precursors and between 80-120% for major ash elements to be acceptable. Balances for an element outside this range requires further investigation and discussion.

Material balances are presented in units of lb/10¹²Btu for trace elements/anion precursors and lb/10⁶Btu for major ash elements to eliminate errors associated with fuel flow and exhaust gas flow measurements from the overall closure results. These emission factor units allow for direct comparisons with measured emission rates from other combustion sources without a concern for generating capacity.

The boiler/ESP mass balance is calculated using the coal feed as the sole input and bottom ash, flyash, and ESP outlet flue gas as the boundary exit points. Two additional secondary material balances are also presented. The boiler mass balance is determined by substituting the ESP inlet for the flyash and ESP outlet exit points. The ESP balance compares the flyash and ESP outlet outputs to the ESP inlet. For purposes of presenting the mass balances, non-detected process stream results are treated at full value.

5.1.5.1 Mass Balances for Trace Elements and Anion Precursors

Trace element and anion precursor mass balance results are presented on Table 5-11 and graphically on Figure 5-1. In general, material balances were excellent for the post-retrofit test program. With the exception of selenium, all trace element/anion precursor balances fell within the 70-130% range, with most balances between 80-115% (the only exception being the cadmium ESP balance at 73%).

Severe negative matrix interferences from the high levels of sulfur found in the ESP inlet and ESP outlet samples tremendously hindered their analyses for selenium. Given that the EPA

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TABLE 5-11

MASS BALANCE FOR TRACE ELEMENTS/ANION PRECURSORS -- BOILER/ESP

NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM

AUGUST 1996

		Mass Flo	ow Rate, lb/10 ¹² I	3tu		Mass Balances, %		
Target Elements	INPUTS	INTERMEDIATE		OUTPUT	S	Boiler		
•	Coal	ESP Inlet	Bottom Ash	Flyash	ESP Outlet	/ESP	Boiler	ESP
Trace Elements								
Antimony	23	23	ND<0.86	20	0.19	91%	102%	88%
Arsenic	515	489	7.8	509	1.73	101%	96%	104%
Barium	5,579	4,869	569	5.005	2.1	100%	97%	103%
Beryllium	60	52	5.0	46	0.03	84%	95%	88%
Cadmium	3.2	3.5	0.066	2.5	ND< 0.04	80%	110%	73%
Chromium	809	689	90	734	0.20	102%	96%	107%
Cobalt	191	183	25	176	0.12	105%	109%	96%
Copper	532	475	<i>5</i> 3	436	0.90	92%	99%	92%
Lead	287	309	10	256	0.56	93%	111%	83%
Manganese	1,439	1,373	201	1,206	0.61	98%	109%	88%
Mercury	7.4	6.89	0.011	0.57	5.74	85%	93%	91%
Molybdenum	110	97	5.8	102	0.39	98%	94%	105%
Nickel	594	528	88	470	0.15	94%	104%	89%
Phosphorus	17,280	17,075	1,923	16,640	66	108%	110%	98%
Selenium	88	26	ND<0.52	19	35	61%	30%	204%
Vanadium	1,201	1,129	120	1,099	1.1	102%	104%	97%
Anion Precursors								
Chlorine	64,238	65,190	111	636	65,159	103%	102%	101%
Fluorine	7,005	6,561	22	169	6,492	95%	94%	102%
Sulfur	1.79E+06	1.87E+06	928	28,336	1.73E+06	98%	104%	94%

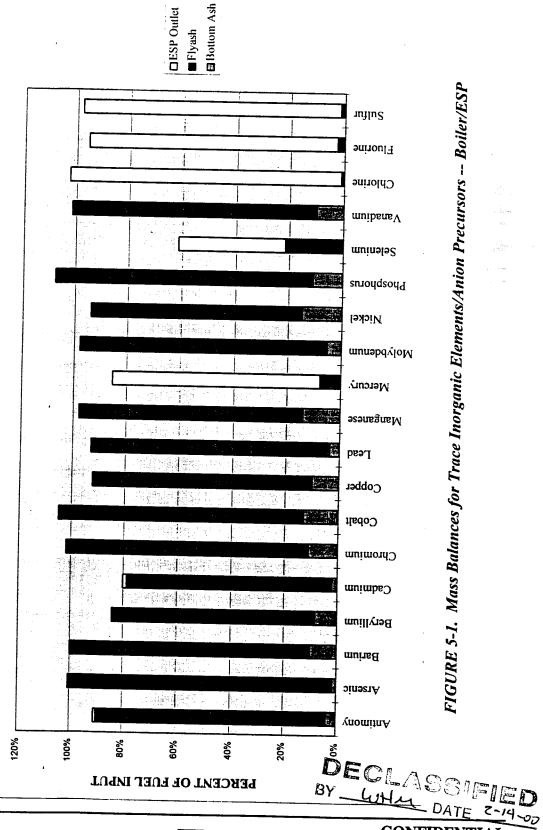
Notes

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(1) Mass Balance, Boiler/ESP = (Bottom Ash + Flyash + ESP Outlet)/Coal

Mass Balance, Boiler = (ESP Inlet + Bottom Ash)/Coal Mass Balance, ESP = (Flyash + ESP Outlet)/ESP Inlet





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NYS1A-11476/R107G404.T Rev. (June 6, 1997) Method 29 results from the May 1994 baseline test program also possessed severe low biases for selenium, it is now believed that sulfur interferences are the main source for the low biases associated with the selenium analytical results for Milliken Unit 2. This would explain why the post-retrofit ESP inlet/outlet and May 1994 baseline selenium data are biased low, and at the same time why no significant matrix interferences were encountered during the analyses of the post-retrofit FGD outlet/stack samples.

From comparisons with coal input and flyash levels, the severe magnitude of the low bias associated with the ESP inlet/outlet selenium results is clear. Based on the selenium coal input of 88 lb/10¹²Btu and the flyash output of 19 lb/10¹²Btu, ESP inlet selenium levels should be in the 80-90 lb/10¹²Btu range as opposed to 26 lb/10¹²Btu, and the ESP outlet selenium results should be on the order of 60-70 lb/10¹²Btu well above the reported 35 lb/10¹²Btu. Coal selenium levels are considered valid for two reasons:

- 1) They agree with Consol's database for the type of coal fired during this test program.
- 2) Most of the sulfur present in the coal will be vaporized during digestion, and therefore will not be present in the digestate used for analysis.

Flyash selenium concentrations are considered valid also for two reasons:

- 1) Both Zenon and EERC analyzed different flyash sample groups using different digestion and analytical techniques, but produced similar results.
- 2) Very little sulfur (<0.5%) is present in the flyash.

Section 5.1.5.3 provides further discussion regarding trace element/anion precursor distribution across the boiler/ESP process streams.

5.1.5.2 Mass Balances for Major Ash Elements

Table 5-12 presents the material balance results for the major ash elements in units of lb/10⁶Btu. All major element balances are within the 80-120% range, with most between 90-110% (the only exceptions being magnesium boiler/ESP and boiler balances of 113% and 116%, respectively). Distribution of the major ash elements across the boiler/ESP output streams normalized to 100% find 88.3% in the flyash, 11.6% in the bottom ash, and 0.1% in the flue gas. This distribution ratio is similar to the ash which showed 87.8% as flyash, 12.1% as bottom ash, and 0.1% as particulate exiting the ESP in the flue gas.



TABLE 5-12
MASS BALANCE FOR MAJOR ASH ELEMENTS -- BOILER/ESP
NYSEG MILLIKEN UNIT'2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

_		Mass Flo	ow Rate, lb/10°B	tu		Mass Balances, %(1			
Target Elements	<u>INPUTS</u>	INTERMEDIATE		OUTPUTS	3	Boiler			
	Coal	ESP Inlet	Bottom Ash	Flyash	ESP Outlet	/ESP	Boiler	ESP	
Major Elements									
Aluminum	0.759	0.675	0.084	0.692	1.6E-04	102%	100%	103%	
Calcium	0.275	0.228	0.040	0.251	2.0E-04	106%	97%	110%	
Iron	0.918	0.821	0.16	0.827	8.5E-05	108%	107%	101%	
Magnesium	0.037	0.037	0.0050	0.036	1.5E-05	113%	116%	97%	
Phosphorus	0.017	0.017	0.0019	0.017	6.6E-05	108%	110%	98%	
Potassium	0.094	0.092	0.009	0.091	2.8E-05	107%	108%	99%	
Silicon	1.42	NA	0.17	1.350	NA.	107%	NA	NA	
Sodium	0.039	0.038	0.0040	0.034	1.1E-04	98%	108%	90%	
Titanium	0.037	0.035	0.0040	0.034	1.1E-05	103%	103%	99%	

NA -- silicon not available from EPA Method 29 sample trains used at the ESP inlet and outlet.

(1) Mass Balance, Boiler/ESP = (Bottom Ash + Flyash + ESP Outlet)/Coal

Mass Balance, Boiler = (ESP Inlet + Bottom Ash)/Coal

Mass Balance, ESP = (Flyash + ESP Outlet)/ESP Inlet



5.1.5.3 Distribution of Trace Elements/Anion Precursors across Boiler/ESP Process Streams

Figure 5-1 illustrated the general distributions of each trace element/anion precursor across the three output streams as a percent of fuel input. Exact distributions are presented on Table 5-13 as a % of total output. Elements are ranked and classified on Table 5-13 based on their volatility according to the following phenomenons:

- 1. Elements found primarily in the ESP outlet exhaust are considered the most volatile. Following vaporization by the combustion process, these elements do not condense on flyash particles and are thus emitted from the ESP outlet fully in the vapor-phase.
- 2. Elements found enriched on the flyash are partially vaporized during the combustion process and later condense on flyash particles. Elements measured at higher percentages in the flyash are considered more volatile than those that exhibited less flyash enrichment.
- 3. Elements that were not enriched in the flyash are the least volatile; the combustion process had no effect on their ash concentrations.

The degree to which an element is enriched in a process stream is determined by the difference between the element's distribution percentage for that stream and that of the reference distribution stream. Dividing the element distribution percentage by the reference percentage given for the major ash elements, relative enrichment ratios (RERs) were calculated for each process stream. These RERs are illustrated in Figure 5-2. A RER greater than one correlates with a species that is enriched in a particular process stream. Species vaporized during the combustion process will later condense on the flyash, with preferential enrichment with decreasing particle size. A RER less than one indicates a species was depleted in an process stream.

Average trace element distribution across the three output streams (excluding mercury, selenium, and anion precursors) was 8.7% in the bottom ash, 91.0% in the flyash and 0.3% in the ESP outlet flue gas.

5.2 FGD SOLID AND LIQUID/SLUDGE STREAM SAMPLE RESULTS

This section begins by defining the material balance boundary around the FGD system. The location of the boundary decides which of the several FGD process are relevant to



TABLE 5-13
RELATIVE DISTRIBUTION OF TRACE INORGANIC ELEMENTS
AS A PERCENT OF TOTAL OUTPUT
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Element	Bottom Ash	Flyash	ESP Outlet
		% of Total Output	
Elements Found Prima		aust:	
Chlorine	0.2%	1.0%	98.9%
Sulfur	0.1%	1.6%	98.3%
Fluorine	0.3%	2.5%	97.1%
Mercury	0.2%	9.0%	90.8%
Selenium	1.0%	34.4%	64.6%
Elements Found Heavily	Enriched in Flyash:		
Arsenic	1.5%	98.2%	0.3%
Lead	3.8%	96.0%	0.2%
Cadmium	2.5%	95.8%	1.7%
Antimony	4.1%	95.0%	0.9%
Molybdenum	5.4%	94.2%	0.4%
Elements Found Slightly	Enriched in Flyash:		
Beryllium	9.8%	90.2%	0.1%
Vanadium	9.9%	90.1%	0.1%
Barium	10.2%	89.8%	0.0%
Phosphorus	10.3%	89.3%	0.4%
Elements Found Equally	Distributed Between	Flyash & Bottom As	sh:
Chromium	10.9%	89.1%	— 0.0%
Copper	10.9%	88.9%	0.2%
Cobalt	12.4%	87.6%	0.1%
Elements Found Enriche	d in Bottom Ash:		
Manganese	14.3%	85.6%	0.0%
lickel	15.8%	84.2%	0.0%
Reference Distributions (1):		
Ash	12.1%	87.8%	0.1%
lajor Ash Elements	11.6%	88.3%	0.1%

Note: (1) Major ash elements distribution used as reference stream to calculate relative enrichment ratios.

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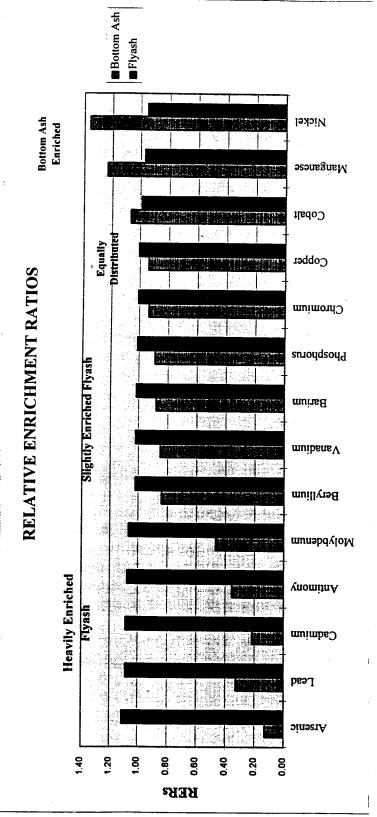


FIGURE 5-2. Relative Enrichment Ratios for Selected Trace Inorganic Elements

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the mass balance study and in what way. Relevant process stream flow rates are then discussed, followed by results presentations for each sample stream, and finally a review of the mass balance data.

5.2.1 FGD Material Balance Overview

Figure 5-3 illustrates the complex relationship between the large number of key FGD process streams. The material balance boundary for Unit 2 chosen for this test program is also illustrated on Figure 5-3. This boundary defined the following process streams as "input" and "output," and required representative samples from these streams to be collected and analyzed for mass balance purposes:

FGD Material Balance Input Streams

- Unit 2 ESP Outlet Flue Gas
- > Limestone Solids
- > PWRF Outlet (to FGD Absorber Module)
- > Significant Chemical Treatment Additives (i.e. lime and FeCl₃)

FGD Material Balance Output Streams

- > Unit 2 FGD Outlet/Stack Flue Gas
- > Gypsum Solids
- > Brine Product
- > FGD Absorber Blowdown/Clarified Water Treatment Sludge

Since only Unit 2 was being examined as part of this test program, only those FGD process streams concerned with the treatment of Unit 2's flue gas were of interest. Limestone solids were considered uniform enough to be sampled without regard as to which unit treatment process they were intended. The gypsum solids produced from the treatment of Unit 2's flue gas were separated out and sampled accordingly. The PWRF outlet, chemical treatment additives, brine product, and FGD sludge process streams are common to the desulfurization of both Unit 1 and Unit 2's flue gas. There was no feasible way to isolate Unit 2 from Unit 1 for these streams, as a result, their flow rates were adjusted proportionally based on net MW production from both units.

5.2.2 Solid and Liquid/Sludge Process Stream Flow Rates and Solids Mass Balance

Table 5-14 presents flow rates for each relevant solid and liquid/sludge input and output FGD process stream on a lb/hr or gpm basis. Similar flow rates are included in the stream of t

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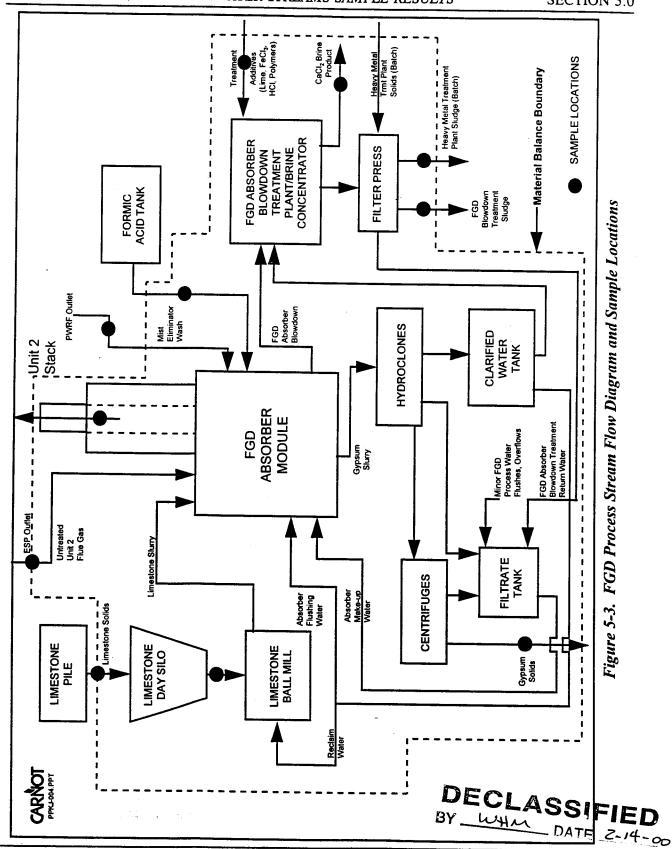


TABLE 5-14
FGD SOLIDS PROCESS STREAM FLOW RATES, POUNDS/HOUR BASIS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

		Flow I	Rate, lb/hr		
Process Stream	Test 1	Test 2	Test 3	Average	_
	Aug.7	Aug. 8	Aug. 9		
Unit 2 Coal Flow (dry)	109.368	113.264	113,940	112,191	
Unit 2 Coal HHV, Btu/lb (dry)	13,731	13,791	13,661	13,728	
FGD Solids Input Streams					
Unit 2 ESP Outlet/FGD Inlet Flue Gas:					
Total Sulfur (as SO ₄ ²⁻)	7.747	8,076	8.089	7,971	
Particulate Matter (PM)	5.8	21.4	7.2	7,971 11	
Limestone Solids	8.204	8.345	7.775	8.108	
PWRF Outlet to Unit 2 ABS Module Solids	38	34	42	38	
FGD Blwdwn/Clarif'd Wtr Trmt Chemical Add'ts	s :			30	
Lime Solids for Unit 2 Only	585	589	664	613	
FeCl ₃ Solids for Unit 2 Only	0.54	0.54	0.61	0.56	
Total Input Solids	16,581	17,067	16,579	16,742	
FGD Solids Output Streams					
FGD Outlet/Stack Flue Gas:					
Total Sulfur (as SO ₄ ²)	711	459	576	582	
Particulate Matter (PM)	20	32	10	21	
Gypsum Solids	15,606	15,878	15,263	15.582	
Brine Product Solids for Unit 2 Only	197	150	147	164	
FGD Sludge for Unit 2 Only (dry basis)	106.2	106.2	106.2	106.2	
Total Output Solids	16,641	16,624	16,103	16,456	
Total Solids Mass Balance	100%	97%	97%	98%	
Sulfur Oxides FGD Removal Efficiency	90.8%	94.3%	92.9%	92.7%	
FGD Liquid Stream Flow Rates, gpm					
PWRF Outlet to Unit 2 ABS Module	289.36	275.78	325.29	296.81	
Brine Product for Unit 2 Only	8.95	7.29	6.83	7.69	

Calculations:

Total Solids Mass Balance = Total Output Solids/Total Input Solids

Total Output Solids = FGD Outlet/Stack Flue Gas Solids (Total Sulfur Oxides and PM) + Gypsum Solids + Brine Product Solids + FGD Sludge

Total Input Solids = ESP Outlet/FGD Inlet Flue Gas Solids (Total Sulfur Oxides and PM) + Limestone Solids + PWRF Outlet Solids

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lb/10⁶Btu or L/10⁶Btu basis. Flow rates on a lb/hr basis are provided to clearly illustrate the magnitude of solids entering and exiting the FGD absorber module, and on an emission factor basis because those flows are used for subsequent mass balance calculations.

FGD operating data logs provided limestone and gypsum slurry rates in gallons per minute, which were converted to lb/hr of total solids using specific gravity and %solids values also supplied by the plant. FGD sludge production weights were converted to a dry, Unit 2 only basis. Limestone, gypsum and sludge sample concentrations for target elements are reported on a dry basis. Mass balance calculations for target elements found in these samples are identical to those outlined in Section 5.1.1 for the ash streams.

For the liquid streams, FGD operating data logs provided flow rates in gallons per minute, which were converted to liters per million Btu for subsequent mass balance calculations. Solids concentration values were applied to FGD liquid stream flow rates to determine their contributions to the solids balance. Given target element concentrations in the liquid streams samples, the following material balance equations were used:

- 1) Analyte Mass Emission, $lb_{(analyte)}/hr = Analyte Concentration$, $mg_{(analyte)}/L_{(liquid stream)}$ * 3.785 L/gal * Liquid Stream Flow Rate, $gal_{(liquid stream)}/min$ * 60 min/hr * lb/454,000mg
- Analyte Emission Factor, $lb_{(analyte)}/10^{12}Btu_{(fuel\ input)} = Analyte Concentration, mg_{(analyte)}/L_{(liquid\ stream)}$ * Liquid Stream Flow Rate, $L_{(liquid\ stream)}/10^6Btu_{(fuel\ input)}$ * lb/454,000mg * 10^6 .
 - 2a) Liquid Flow Rate, L/10⁶Btu = gpm * 3.785 L/gal * 60 min/hr * $1/lb_{(Unit 2)}$ fuel/hr * 1/HHV * 10^6

For the chemical additive streams, typical flow rates, %solids (i.e. CaO or FeCl₃), and specific gravities were obtained from plant personnel to calculate solids, calcium, iron, and chlorine input rates.

FGD process stream flow rate raw data and calculations are given in Appendix C.

As shown on Tables 5-14 and 5-15, an FGD solids mass balance was calculated using sulfur oxide and particulate matter levels in the flue gas as their only significant solids content. Total solids mass balance results were excellent, averaging 98%, which indicates that there is no significant bias associated with any of the major flow rate measurements. 48% of total input solids is from sulfur oxides and 52% comes from the limestone slurry. The output solids are distributed as 3.5% sulfur oxides, 95% gypsum solids, 1% brine solids, and 0.5% sludge.

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TABLE 5-15
FGD SOLIDS PROCESS STREAM FLOW RATES, EMISSION FACTOR BASIS
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

	Flow Rate, lb/10 ⁶ Btu					
Process Stream	Test 1	Test 2	Test 3	Average		
	Aug.7	Aug. 8	Aug. 9			
Unit 2 Coal Flow, lb/hr (dry)	109,368	113.264	113,940	112,191		
Unit 2 Coal HHV, Btu/lb (dry)	13,731	13,791	13,661	13,728		
FGD Solids Input Streams						
Unit 2 ESP Outlet/FGD Inlet Flue Gas:						
Total Sulfur (as SO ₄ ² -)	5.18	5.17	5.18	5.18		
Particulate Matter (PM)	0.004	0.014	0.004	0.007		
Limestone Solids	5.46	5.34	5.00	5.26		
PWRF Outlet to Unit 2 ABS Module Solids	0.025	0.022	0.027	0.025		
FGD Blwdwn/Clarif'd Wtr Trmt Chemical Add't	s:					
Lime Solids for Unit 2 Only	0.39	0.38	0.43	0.40		
FeCl ₃ Solids for Unit 2 Only	0.0004	0.0003	0.0004	0.0004		
Total Input Solids	11.06	10.93	10.64	10.87		
FGD Solids Output Streams						
FGD Outlet/Stack Flue Gas:						
Total Sulfur (as SO ₄ ²)	0.44	0.28	0.35	0.36		
Particulate Matter (PM)	0.013	0.021	0.007	0.014		
Gypsum Solids	10.39	10.16	9.81	10.12		
Brine Product Solids for Unit 2 Only	0.131	0.096	0.094	0.107		
FGD Sludge for Unit 2 Only (dry basis)	0.071	0.068	0.068	0.069		
Total Output Solids	11.04	10.63	10.33	10.66		
Total Solids Mass Balance	100%	97%	97%	98%		
Sulfur Oxides FGD Removal Efficiency	91.6%	94.6%	93.2%	93.1%		
FGD Liquid Stream Flow Rates, L/10 ⁶ Btu						
PWRF Outlet to Unit 2 ABS Module	43.76	40.10	47.46	43.77		
Brine Product for Unit 2 Only	1.35	1.06	1.00	1.13		

Calculations:

Solids Flow Rate, $lb_{solids}/10^6$ Btu = $lb_{solids}/hr * 1/lb_{(Unit 2 fuel)}/hr * 1/HHV * 10^6$

Liquids Flow Rate, $L/10^6$ Btu = gpm * 3.785 L/gal * 60 min/hr * $1/lb_{(Unit 2 fuel)}$ /hr * 1/HHV * 10^6

Total Solids Mass Balance = Total Output Solids/Total Input Solids

Total Output Solids = FGD Outlet/Stack Flue Gas Solids (Total Sulfur Oxides and PM) + Gypsum Solids +
Brine Product Solids + FGD Sludge

Total Input Solids = ESP Outlet/FGD Inlet Flue Gas Solids (Total Sulfur Oxides and PM) + Limestone Solids + PWRF Outlet Solids

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5.2.3 <u>Limestone Solids</u>

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Table 5-16 reports the ultimate analyses results of the limestone and gypsum solids. The limestone was found to contain almost 60% ash.

The inorganic element analysis of the limestone is given on Table 5-17. Antimony, arsenic, barium, beryllium, cobalt, copper, and selenium were not detected in the limestone. Predominant elements include manganese for the trace elements, magnesium and silicon for the major elements (excluding calcium), and sulfur for the anion precursors. The limestone was determined to be almost 40% calcium. Notable variability between replicates is seen for molybdenum, fluorine and sulfur.

5.2.4 Gypsum Solids

As shown on Table 5-16, the gypsum solids were found to contain almost 80% ash.

Table 5-18 presents the inorganic elemental analyses of the gypsum. Antimony, arsenic, barium, beryllium, cobalt, copper, and vanadium were not detected in the gypsum. Besides calcium and sulfur, predominant elements in each class include manganese and chromium, silicon, magnesium, and iron and fluorine. For most detected elements, 2-GYPSUM contained higher levels of them than the other two replicates. This suggests that the "batch" processing of gypsum may have added a significant bias to the representative nature of the samples collected. It is not expected that a representative sample of a 24 hour gypsum production cycle will vary this much in composition from day to day considering the relatively uniform limestone composition.

5.2.5 PWRF Outlet

Results for the PWRF outlet samples are provided on Table 5-19. Of the trace elements, only arsenic, barium, cadmium, and copper were detected. Iron, phosphorus, and titanium were not detected for the major elements. Water soluble elements (i.e. Ca, Cl, S, Na, Mg, and K) were predominantly found in the PWRF outlet process water.

5.2.6 Brine Product

Table 5-20 present the target element analyses of the brine product samples. Antimony, arsenic, cobalt, copper, mercury, molybdenum, selenium, vanadium, aluminum, and silicon were not detected in the brine. Chlorine and calcium were the predominant elements found.

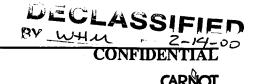


TABLE 5-16
LIMESTONE & GYPSUM SOLIDS ULTIMATE ANALYSIS REPORT
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number Sample Date Sampe Time	1-Limestone 8/7/96 1830	2-Limestone 8/8/96 1330	3-Limestone 8/9/96 1430	Average	1-Gypsum 8/7/96 821/1429	2-Gypsum 8/8/96 930/1330	3-Gypsum 8/9/96 1005/1445	Average
Ultimate Analysis (Dry B	asis):							
%Carbon	11.55	11.55	11.55	11.55	0.50	0.69	0.29	0.49
%Hydrogen	0.16	0.10	0.11	0.12	1.31	1.04	1.21	1.19
%Nitrogen	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
%Sulfur	0.16	0.30	0.36	0.273	18.35	17.40	18.00	17.92
%Ash (@550°C)	59.57	59.33	59.12	59.34	79.82	80.85	80.49	80.39
%Oxygen	28.55	28.71	28.85	28.70	0.00	0.00	0.00	0.00
Total Moisture, %	1.23	1.05	2.58	1.62	8.75	8.93	8.27	8.65
Air Dry Loss, %	1.21	1.02	2.54	1.59	6.54	6.72	5.94	6.40
As-Det./Res. Moisture, %	0.02	0.03	0.04	0.03	2.36	2.37	2.48	2.40

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TABLE 5-17
INORGANIC ELEMENT ANALYSIS -- LIMESTONE
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-LIMESTO	NE 2-LIMESTO	NE 3-LIMESTO	NE	AVERAG	E	Unce	ertainty
Date	8/7/96	8/8/96	8/9/96					5%CI
Limestone Flow Rate,	lb/hr 8,204	8,345	7,775					
Limestone Rate, lb/10	⁶ Btu 5.46	5.34	5.00					
Total Moisture, %	1.23	1.05	2.58					
As Det. Moisture, %	0.02	0.03	0.04					
Element	mg/kg	mg/kg	mg/kg	mg/kg	lb/hr	lb/10 ¹² Btu	%	mg/kg
-		Dry	Basis					
Trace Elements								
Antimony	ND< 1	ND< 1	ND< 1	ND< 1	ND< 0.0081	ND< 5.3		
Arsenic	ND< 0.4	ND< 0.4	ND< 0.4	ND< 0.4	ND< 0.0031	ND< 2.1		
	ND< 2.0	ND< 2.0	ND< 2.0	ND< 2.0	ND< 0.0032 ND< 0.016	ND< 2.1 ND< 11		
	ND< 0.1	ND< 0.1	ND< 0.1	ND< 0.1	ND< 0.0008	ND< 0.53		
Cadmium	0.23	0.29	0.29	0.27	0.0022	1.4	32%	0.09
Chromium	1.1	1.1	1.2	1.1	0.0022	6.0	13%	0.09
Cobalt	ND< 0.4	ND< 0.4	ND< 0.4	ND< 0.4	ND< 0.0032	ND< 2.1		0.1
	ND< 2	ND< 2	ND< 2	ND< 2	ND< 0.0032	ND< 11		
Lead	0.21	0.24	0.25	0.23	0.0019	1.2	22%	0.05
Manganese	42.7	42.0	40.7	41.8	0.34	220	6%	2.5
Mercury	0.002	ND< 0.002	0.020	0.008	6.0E-05	0.039	346%	0.027
Molybdenum	0.21	0.25	0.651	0.370	0.0030	1.9	164%	0.606
Nickel	1.47	1.46	1.62	1.52	0.012	8.0	15%	0.000
Selenium	ND< 0.04	ND< 0.04	ND< 0.04	ND< 0.04	ND< 0.0003	ND< 0.21		0.22
Vanadium	1.8	1.8	1.9	1.8	0.015	9.7	8%	0.1
Major Elements			•>	1.0	0.015	3.7	070	0.1
Aluminum	2,365	2,355	2,347	2,355	19.1	12,407	1%	22
Calcium	3.95E+05	•	3.97E+05	3.97E+05	3,217	2.09E+06	1%	4,368
Iron	3,125	3,112	3,101	3,113	25	16,397	1%	29
Magnesium	6,358	6,440	6,417	6,405	52	33,733	2%	105
Phosphorus	910	880	851	881	7.1	4,642	8%	73
Potassium	148	148	147	148	1.20	778	1%	1
Silicon	5,207	5,186	5,168	5,187	42	27,322	1%	49
Sodium	2,077	1,849	2,412	2,113	17	11,091 -	33%	704
Titanium	71	71	71	71	0.58	375	1%	1
Anion Precursors	•	•	- 3	- -	3.00	2.0		•
Chlorine	101	101	103	102	0.82	535	3%	3
Fluorine	526	202	452-	393	3.2	2070	107%	421
Sulfur	1,288	4,134	2,770	2,731	22.2	14,320	129%	3,534

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TABLE 5-18
INORGANIC ELEMENT ANALYSIS -- GYPSUM
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-GYPSUI	M 2-GYPSUN	A 3-GYPSUM		AVERA	ìE.	Line	ertainty
Date	8/7/96	8/8/96	8/9/96					95%CI
Gypsum Flow Rat	e, lb/hr 15,606	15,878	15,263	•				73 /6C1
Gypsum Rate, lb/1	0 ⁶ Btu 10.39	10.16	9.81					
Total Moisture, %	8.75	8.93	8.27					
As Det. Moisture,	% 2.36	2.37	2.48					
Element	mg/kg	mg/kg	mg/kg	mg/kg	lb/hr	lb/10 ¹² Btu	%	mg/kg
			Basis		-	.b/10 Btu	/0	mg/ kg
Trace Elements								
Antimony	ND< 1.0	ND< 1.0	ND< 1.0	ND - 10	MD - 0.046			
Arsenic	ND< 0.41	ND< 0.41	ND< 1.0 ND< 0.41	ND< 1.0	ND< 0.016	ND< 10		
Barium	ND< 7.2	ND< 7.2		ND< 0.41	ND< 0.0064	ND< 4.1		
Beryllium	ND< 0.51	ND< 7.2 ND< 0.51	ND< 7.2	ND< 7.2	ND< 0.11	ND< 73		
Cadmium	0.086	0.236	ND< 0.51	ND< 0.51	ND< 0.0080	ND< 5.2		
Chromium	1.6	0.236 2.7	0.090	0.14	0.0022	1.4	154%	0.21
Cobalt	ND< 0.41		1.6	2.0	0.031	20	74%	1.5
Copper	ND< 0.41 ND< 6.1	ND< 0.41	ND< 0.41	ND< 0.41	ND< 0.0064	ND< 4.1		
Lead		ND< 6.1	ND< 6.2	ND< 6.1	ND< 0.096	ND< 62		
	0.26	0.47	ND< 0.21	0.28	0.0043	2.8	166%	0.46
Manganese	2.9	4.3	2.3	3.1	0.049	32	83%	2.6
Mercury	0.177	0.469	0.144	0.263	0.0041	2.7	169%	0.445
Molybdenum	0.58	0.78	0.78	0.71	0.011	7.2	39%	0.28
Nickel	0.81	1.33	0.75	1.0	0.015	10	83%	0.8
Selenium	0.41	0.51	0.41	0.44	0.0069	4.5	33%	0.15
Vanadium	ND< 4.1	ND< 4.1	ND< 4.1	ND< 4.1	ND< 0.064	ND< 41		
<u> Major Elements</u>								
Aluminum	1,099	1,249	1,170	1,173	18	11.865	16%	186
Calcium	2.31E+05	2.46E+05	2.28E+05	2.35E+05	3,665	2.38E+06	10%	24,329
Iron	1,788	1,821	1,799	1,803	28	18,247	2%	42
Magnesium	1,831	3,141	2,036	2,336	37	23,639	75%	1,749
Phosphorus	837	923	842	867	14	8,780	14%	121
Potassium	66	68	67	67	1.04	677	2%	2
Silicon	1,867	3,538	2,687	2,697	42	27,237	77%	2,073
Sodium	296	302	298	299	4.7	3,024	2%	2,073 7
Titanium	24	49	48	40	0.63	406	2% 87%	, 35
Anion Precursors				•••	0.03	400	0/70	33
Chlorine	110	110	109	110	1.7	1,110	1%	
Fluorine	723	999	654	792	1.7			1
Sulfur	1.83E+05	1.72E+05	1.82E+05	1.79E+05	2,784	8,027 1.81E+06	57% 8%	453 15,117



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TABLE 5-19
INORGANIC ELEMENT RESULTS SUMMARY-- PWRF OUTLET TO UNIT 2 ABS MODULE
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number		1-PWRF	2-PWRF	3-PWRF		AVERAGE		Unc	ertainty
Sample Date		8/7/96	8/8/96	8/9/96	***************************************		···	-	5%CI
PWRF Flow Rate, gpn	1	289.36	275.78	325.29					
PWRF Flow Rate, L/1	0 ⁶ Btu	43.76	40.10	47.46					•
рН (20°C)		8.16	8.12	8.15	. •				
Alkalinity (as CaCO ₃),	mg/L	100	100	100					
Hardness (as CaCO ₃),		140	150	150					
TDS (180°C), mg/L		260	250	260					
TSS, mg/L		<4.2	<4.2	· <4.2					
Element	п	ng/L	mg/L	mg/L	mg/L	lb/hr	lb/10 ¹² Btu	%	mg/L
Trace Elements					· !! - ,				
Antimony	ND<	0.0020	ND< 0.0020	ND< 0.0020	ND< 0.0020	ND< 3.0E-04	ND< 0.19		
Arsenic		0.0020	0.0029	0.0024	0.0020	3.1E-04	0.19 0.20	 116%	0.001
Barium		0.031	0.035	0.0024	0.0021	0.00495	0.20 3.2	16%	
Beryllium	ND<	0.001	ND< 0.001	ND< 0.001	ND< 0.001	ND< 1.5E-04	3.2 ND< 0.096	10%	0.005
Cadmium		0.0001	0.0002	ND< 0.0001	0.0001	1.4E-05	0.0092		
Chromium		0.004	ND< 0.004	ND< 0.004	ND< 0.004	ND< 5.9E-04	ND< 0.39	143%	0.000
Cobalt	_	0.004	ND< 0.011	ND< 0.004	ND< 0.004 ND< 0.011	ND< 0.00163	ND< 0.39		
Copper	.,,,,	0.009	0.012	0.010	0.010	0.00163	0.99	 2 7 9/	
Lead	ND<	0.0010	ND< 0.0010	ND< 0.0010	ND< 0.0010	ND< 1.5E-04	0.99 ND< 0.096	37%	0.004
Manganese		0.007	ND< 0.0010	ND< 0.0010	ND< 0.0010	ND< 1.3E-04 ND< 0.0010			
Mercury		5E-05	ND< 5E-05	ND< 5E-05	ND< 0.007 ND< 5E-05		ND< 0.67		
Molybdenum		0.011	ND< 0.011	ND< 0.011		ND< 7.4E-06	ND< 0.0048		
Nickel		0.011	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.00163	ND< 1.1		-
Selenium		0.0020	ND< 0.011	ND< 0.0010	ND< 0.011	ND< 0.00163	ND< 1.1		
Vanadium		0.0020	ND< 0.0020 ND< 0.006	ND< 0.0020	ND< 0.0020 ND< 0.006	ND< 3.0E-04	ND< 0.19		
Maior Elements	ND-	0.000	ND~ 0.000	0.006	ND~ 0.006	ND< 8.9E-04	ND< 0.58		
Aluminum		0.34	0.43	0.44	0.40	0.000	10	2.407	
Calcium		41	45	45	0.40 44	0.060	39	34%	0.14
Iron	ND-	0.011	ND< 0.011	ND< 0.011	ND< 0.011	6.5 ND< 0.00163	4210	13%	6
Magnesium	ND.	9.6	10	10	9.9		ND< 1.1 951		-
Phosphorus	ND	0.066	0.073	ND< 0.060	9.9 ND< 0.066	1.5 ND< 0.0098	951 ND< 6.4	6%	0.6
Potassium	ND.	1.9	2.5	2.4	2.3			250/	~-
Silicon		0.30	0.59	0.57	2.3 0.49	0.34 0.073	218 47	35% 83%	0.8 0.40
Sodium		23	25	26	25	3.7	47 2381		
Titanium	ND<	0.011	ND< 0.011	ND< 0.011	ND< 0.011	3.7 ND< 0.00163	ND< 1.1	15%	4
nion Precursors	ישיי	J.VII	0.011	110 - 0.011	14D > 0.011	0.00100	1.1 ~UP		
Chloride		43	42	42	42	6.3	4082	3%	1
Fluoride		0:12	0.09	0.09	0.10	0.015	10	3% 43%	0.04
Sulfate (as SO ₄ ²)		34	36	42	37	5.6	3616		
Nitrite (as N)	ND<	-	ND< 0.05	ND< 0.05	ND< 0.050			28%	10
Nitrate (as N)	אטא	1.0	1.0	1.0	1.0	ND< 0.00742 0.15	ND< 4.8 96	 0%	0.0

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TABLE 5-20
INORGANIC ELEMENT RESULTS SUMMARY-- BRINE PRODUCT
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-BRIN	E 2-BRINE	3-BRINE		AVERAGE		Unc	ertainty
Sample Date	8/7/96	8/8/96	8/9/96		·			95%CI
Brine Flow Rate, gpi	n 8.95	7.29	6.83					
Brine Flow Rate, L/1	0 ⁶ Btu 1.35	1.06	1.00					
Element	mg/L	mg/L	mg/L	mg/L	lb/hr	lb/10 ¹² Btu	%	mg/L
Trace Elements								
Antimony	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.0000	ND< 0.03	••	
Arsenic	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.0000	ND< 0.03		
Barium	0.96	0.98	0.96	0.97	0.004	2.4	3%	0.03
Beryllium	0.002	ND< 0.001	ND< 0.001	0.001	4.2E-06	0.003	215%	0.002
Cadmium	0.0015	ND< 0.0001	ND< 0.0001	0.0005	2.4E-06	0.003	390%	0.002
Chromium	0.011	0.010	0.010	0.010	0.0000	0.002	14%	0.002
Cobalt	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.011	ND< 4.2E-05	ND< 0.03		0.001
Copper	0.006	ND< 0.006	ND< 0.006	ND< 0.006	ND< 2.3E-05	ND< 0.03		
Lead	0.0039	0.0023	0.0040	0.0034	1.3E-05	0.009	70%	0.0024
Manganese	0.014	0.049	0.009	0.024	0.0001	0.06	225%	0.0024
Mercury	ND< 5E-05	ND< 5E-05	ND< 5E-05	ND< 5E-05	ND< 2E-07	ND< 0.0001		
Molybdenum	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.011	ND< 4.2E-05	ND< 0.03		
Nickel	0.074	0.076	0.037	0.062	0.00024	0.16	87%	0.055
Selenium	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.0110	ND< 0.0000	ND< 0.03		
Vanadium	ND< 0.006	ND< 0.006	ND< 0.006	ND< 0.006	ND< 2.3E-05	ND< 0.015		
Major Elements								
Aluminum	ND< 0.33	ND< 0.33	ND< 0.33	ND< 0.33	ND< 0.00127	ND< 0.8		
Calcium	15,000	16,000	15,000	15.333	59	38.332	9%	1,433
Iron	0.017	0.097	ND< 0.011	0.040	0.00015	0.10	311%	0.124
Magnesium	28	63	4.3	32	0.12	80	231%	73
Phosphorus	110	120	120	117	0.4	290	12%	14
Potassium	91	83	84	86	0.33	216	13%	11
Silicon	ND< 0.55	ND< 0.55	ND< 0.55	ND< 0.55	ND< 0.002	ND< 1.4		_
Sodium	790	820	750	787	3.0	1972	11%	87
Titanium	0.18	0.18	0.17	0.18	- 0.00068	0.4	8%	0.01
Anion Precursors		•						٠.٠٠
Chloride	28,000	24,000	27,000	26,333	102	66,255	20%	5,168
Fluoride	1.1	0.1	1.3	1.1	0.004	2.8	33%	0.4
Sulfate (as SO ₄ ² 7)	1,000	1,000	980	993	3.8	2489	3%	29

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5.2.7 FGD Sludge

Duplicate FGD sludge sample results are given on Table 5-21. Only antimony, beryllium, cobalt, and vanadium were not detected. Good agreement between replicate results can be seen for all elements found in this semi-solid process stream. The sludge was determined to be 15.5% calcium, 14.5% magnesium, and 4% chloride.

5.2.8 FGD Mass Balance

Unlike the boiler/ESP mass balance, obtaining closure for trace elements around the FGD process is complicated by the following factors:

- 1) Most trace elements exist at low levels (<25 lb/10¹²Btu) in the FGD input streams.
- 2) There are more input (3 total) and output (4 total) streams to be quantified.
- Many of the individual FGD process systems operate in batch cycles (e.g. gypsum and sludge production) with relatively long frequencies. Collecting samples of their output streams over an 8-hour test window may not entirely provide a representative snapshot of actual trace element output rates.
- Analytical detection limits for trace elements in limestone and gypsum samples are generally higher than those seen for coal and ash samples since these matrices can not be equivalently concentrated prior to digestion and analysis. Furthermore, high levels of calcium and sulfur in these samples require sample dilution for some target trace elements. As a result, detection limits for these elements exceed their flue gas concentration levels.

FGD mass balance results are presented on Table 5-22 in units of lb/10¹²Btu. After reviewing the mass balance results, the following observations were made:

- Excellent FGD balances can be seen for trace and major elements (including anion precursors) existing in the ESP outlet flue gas at levels above 1 lb/10¹²Btu. For trace elements above this level in which an FGD balance could be reported, namely arsenic and mercury, balances ranged from 92-107%; for the major elements (excluding phosphorus and sodium), balances were consistently between 93-112%; and for the anion precursors, FGD closures fell within 97-102%.
- As discussed in Sections 4.3 and 5.1.5.1, the ESP outlet selenium level is severely biased low due to severe matrix interferences from sufficient the low levels

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TABLE 5-21
INORGANIC ELEMENT RESULTS SUMMARY-- FGD SLUDGE
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
AUGUST 1996

Test Number	1-FGD Sludge	2-FGD Sludge	AVERAGE	Relative
Sample Date Sludge Flow Rate, lb/hr	8/7/96 106.2	8/8/96 106.2	· · · · · · · · · · · · · · · · · · ·	Percent
Sludge Flow Rate, lb/10 ⁶ Btu	0.07	0.07	•	Diff.
Moisture, %	64	62		

Element	mg/kg	mg/kg	mg/kg	lb/hr	lb/10 ¹² Btu	
		Dry Basis				
Trace Elements						
Antimony	ND< 0.3	0.30	ND< 0.30	ND< 3.2E-05	ND< 0.021	
Arsenic	2.6	2.9	2.8	2.9E-04	0.19	110/
Barium	18	18	18	0.00191	1.3	11%
Beryllium	ND< 0.2	ND< 0.2	ND< 0.2	ND< 2.1E-05	ND< 0.014	0%
Cadmium	1.5	2.5	2.0	2.1E-04	0.14	500/
Chromium	17	16	17	0.0018	0.14 1.1	50%
Cobalt	ND< 10	ND< 10	ND< 10	ND< 0.00106	1.1 ND< 0.70	6%
Copper	15	15	15	0.0016		
Lead	2.3	4.2	3.3	3.5E-04	1.0	0%
Manganese	1700	1600	1650	3.5E-04 0.18	0.22	58%
Mercury	4.8	4.2	4.5		115	6%
Molybdenum	5.0	5.0	5.0	4.8E-04	0.31	13%
Nickel	89	83	3.0 8 6	5.3E-04	0.35	0%
Selenium	24	22	23	0.009	6.0	7%
Vanadium	ND< 20	ND< 20	ND< 20	0.0024	1.6	9%
Major Elements	112 20	ND 1 20	ND~ 20	ND< 0.0021	ND< 1.4	
Aluminum	2200	2500	2350	0.05		
Calcium	130,000	180,000		0.25	163	13%
Iron	4,900	4,700	155,000	16	10,735	32%
Magnesium	150,000	140,000	4,800	0.51	334	4%
Phosphorus	120	140,000	145,000	15	10,085	7%
Potassium	780	810	130	0.014	9	15%
Silicon	370		795	0.08	55	4%
Sodium	1300	560	465	0.049	32	41%
Titanium	87	1300	1300	0.14	90	0%
nion Precursors	8/	96	92	0.010	6.4	10%
Chloride	- 42,000	26.000				
Fluoride	43,000	36,000	39,500	4.2	2,751	18%
	3900	3500	3700	0.39	257	11%
Sulfate (as SO ₄ ²)	4500	4600	4550	0.48	316	2%

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MASS BALANCE FOR TARGET INORGANIC ELEMENTS -- FGD PROCESS **NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM AUGUST 1996** TABLE 5-22

Farret Elements		INPIT STREAMS			OITTDIT CTDEAME	TDEAME		IVIESS TO 10 (2)(3)
	PCD 0(124	I tenestone	Pilit O. Ala		COLLOS	IKEAMS		Balance, %
		Limestone	rwkr Outlet	Gypsum	Brine Product	FGD Sludge	Stack	FGD
Frace Elements								
Antimony	0.19	ND< 5.3	ND< 0.19	ND< 10	ND< 0.03	ND< 0.021	ND< 0.08	Z
Arsenic	1.7	ND< 2.1	0.20	ND< 4.1	ND< 0.03	0.19	160	107%
Barinm	2.1	ND<	3.2	ND< 73	2.4	-	12:	X X
Beryllium	0.03	ND< 0.53	ND< 0.096	ND< 5.2	0.003	ND< 0.014	200	C V
Cadminm	ND< 0.04	1.4	0.0092	1.4	0.002	0.14	0.05	100%
Chromium	0.20	0.9	ND< 0.39	20	0.03	=	0.15	327%
Cobalt	0.12	ND< 2.1	ND<	ND< 4.1	ND< 0.03	ND< 0.70	0.12	Ý.
Copper ⁽¹⁾	06:0	ND<	0.99	ND< 62	ND< 0.015	1.0	69.0	95%
Lead	0.56	1.2	ND< 0.096	2.8	0.00	0.22	0.63	201%
Manganese	0.61	220	ND< 0.67	32	90:0	115	6.1	%19
Mercury	5.74	0.039	ND< 0.0048	2.67	ND< 0.0001	0.31	2.31	92%
Motybdenum	0.39	1.9	ND<	7.2	ND< 0.03	0.35	0.35	280%
Nickel	0.15	0.8	ND< 1.1	0	0.16	0.9	0.33	188%
Selenium	35	ND< 0.21	ND< 0.19	4.5	ND< 0.03	1.6	21	16%
Vanadium	Ξ	6.7	ND< 0.58	ND< 41	ND< 0.015	ND< 1.4	69.0	X
Major Elements								
Aluminum	155	12,407	39	11,865	ND < 0.8	163	19	%96
Calcium ⁽⁴⁾	961	2.37E+06	4210	2.38E+06	38,332	10,735	259	102%
Iron ⁽⁴⁾	82	16,523	ND II	18,247	0.10	334	27	112%
Magnesium	15	33,733	156	23,639	8 0	10,085	104	%86
Phosphorus	9.59	4,642	ND< 6.4	8,780	290	6	15	193%
Potassium	99	778	218	<i>LL</i> 9	216	55	ND< 38	93%
Silicon	ď	27,322	47	27,237	ND< 1.4	32	ā	100%
Sodium	108	160,11	2381	3,024	1972	96	141	38%
Titanium Anion Precursors	11.5	375	ND< 1.1	406	0.4	6.4	6.3	108%
Chlorine ⁽⁴⁾	65,190	775	4082	1,110	66,255	2.751	398	%101
Fluorine	6,561	2070	9	8,027	2.8	257	88	%26
Sulfir	1 875104	14 120	1205	1 815+04	930			

NP -- sample not analyzed for target parameter NA -- not applicable, major input and output streams not detected

(1) For copper the limestone and gypsum streams were treated as zero for calculating their mass balances.

(2) FGD Mass Balance (Outputs/Inputs) = (Gypsum + Brine Product + FGD Sludge + Stack)/(ESP Outlet + Limestone Slurry + PWRF Outlet)

(3) Not detected process stream results divided by two for mass balance calculations.
(4) The calcium, iron, and chloride input flow rates for the lime and ferric chloride chemical treatment additive streams were added to the limestone input rate.

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of sulfur contained in the stack EPA Method 29 samples and the lack of matrix interferences encountered during analysis, the stack selenium results are considered valid. FGD mass balance results will not support the currently reported stack selenium level if the ESP outlet results are actually around 60-70 lb/10¹²Btu (based on coal and flyash levels). It is believed, however, that the gypsum selenium results are also severely biased low due to the large amounts of sulfur (about 18%) present in these samples. This would resolve the FGD balance for selenium given the expected ESP outlet selenium concentration range of 60-70 lb/10¹²Btu.

- Mercury levels found in the gypsum confirm the reported FGD mercury removal efficiency of 60%.
- Non-detected results for antimony, barium, beryllium, cobalt, and vanadium in the limestone and/or gypsum solids precluded the presentation of an FGD mass balance for them.
- Extremely high balances reported for chromium, molybdenum, and nickel ranging from 188-327%, in addition to a higher iron balance than most other major elements of 111%, suggests the likelihood that corrosion of FGD process system surfaces from contact with the acid gas components of the reduced temperature flue gas is a significant input source of these metals for the FGD balance.
- The reason for the high lead FGD balance of 201% could be the high variability in the gypsum lead results, which possess an uncertainty of 166% as a mix of detectable and not-detectable measurements.
- The reason behind the low manganese FGD balance (67%) may be due to the FGD sludge process stream which accounted for 77% of total manganese FGD output. Uncertainties regarding sludge sample representativeness, stemming from the fact that both Unit 1 and Unit 2 contribute to the sludge, and that sludge production operates in batch cycles, will be more profound for elements such as manganese since it is one of the predominant elements found in the sludge.
- The poor balances for phosphorus (193%) and sodium (38%) most likely stem from non-representative or inaccurate analyses of key input and output process stream samples, namely limestone, gypsum and the brine product (for sodium only).



The limestone was a significant input source of most target parameters with the exception of mercury, chlorine, and sulfur. The PWRF was a significant input stream for barium, copper, potassium, sodium, and chlorine. Most target parameters were found in the gypsum solids at significant levels except for chlorine. The brine product was an important output stream for barium, calcium, sodium, and chlorine. For the sludge, barium, chromium, copper, lead, manganese, molybdenum, nickel, selenium, magnesium, and chlorine were found at significant levels.

5.3 WASTEWATER TREATMENT PLANT PROCESS STREAM RESULTS

The primary objective of the WWTP sampling was to determine its effectiveness at removing heavy metals from the coal pile run-off. A secondary objective was to characterize the output streams of the WWTP. All WWTP process stream sampling was performed in duplicate by plant personnel. A complete balance around the plant was outside the scope of this project. As such, several chemical treatment additive streams were not characterized, leaving the WWTP removal efficiencies of certain water soluble elements understated. The wastewater treatment plant process stream results are presented on the following tables:

Table 5-23: Wastewater Treatment Plant Sample Results -- WWTP Inlet

Table 5-24: Wastewater Treatment Plant Sample Results -- WWTP Outlet

Table 5-25: Wastewater Treatment Plant Sample Results -- Coal Pile Run-Off and WWTP Sludge

Table 5-26: Wastewater Treatment Plant Results Summary

Highlights from these tables are listed below:

- The WWTP inlet stream is mostly composed of coal pile run-off, which is the main source of most target inorganic elements seen in the inlet stream. Predominant elements found in the WWTP inlet included manganese for the trace elements, calcium, sodium, and iron for the major elements, and sulfate for the anion precursors. Only antimony, mercury, and nitrite were not detected in the inlet stream.
- For the WWTP outlet stream, only barium, copper, and manganese were detected for the trace elements. Most major elements and anion precursors were detected, with the exceptions being titanium and nitrite.
- Although no flow rates were determined for the coal pile run-off and WWTP sludge streams, it is clear from their target element concentration results that the

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TABLE 5-23 WASTEWATER TREATMENT PLANT SAMPLE RESULTS - WWTP INLET NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **SEPTEMBER 1996**

Test Number	1-WWTP-I	N 2-WWTP-IN	AV	ERAGE	Relative
Sample Date	9/9/96	9/9/96			Percent
Sample Time	1600/2400	1600/2400			Diff.
Flow Rate, gpm	45.0	45.0			
pH (20°C)	2.88	2.87			
Alkalinity (as CaCO ₃		<1.4	•		
Hardness (as CaCO ₃)	, mg/L 1,800	1,800			
TDS (180°C), mg/L	5,800	5,900			
TSS, mg/L	540	550			
Element	mg/L	mg/L	mg/L	lb/hr	
Trace Elements					
Antimony	ND< 0.033	ND< 0.033	ND< 0.033	ND< 7.4E-04	
Arsenic	0.022	0.021	0.022	4.8E-04	5%
Barium	0.071	0.067	0.069	0.00155	5% 6%
Beryllium	0.013	0.014	0.014	3.0E-04	0% 7%
Cadmium	0.0068	0.0068	0.0068	1.5E-04	0%
Chromium	0.032	0.035	0.034	7.5E-04	9%
Cobalt	0.31	0.31	0.31	0.0070	9% 0%
Copper	0.12	0.12	0.12	0.0070	0% 0%
Lead	0.0026	0.0026	0.0026	5.9E-05	0%
Manganese	4.3	4.3	4.3	0.097	0%
Mercury	ND< 5.0E-05	ND< 5.0E-05	ND< 5.0E-05	ND< 1.1E-06	
Molybdenum	0.030	0.029	0.030	6.6E-04	3%
Nickel	0.67	0.68	0.68	0.015	1%
Selenium	0.015	0.013	0.014	3.2E-04	14%
Vanadium	0.007	800.0	0.008	1.7E-04	13%
<u> Iajor Elements</u>			-1000	1.72 04	1370
Aluminum	63	62	63	1.4	2%
Calcium	580	580	580	13	0%
Iron	210	210	210	4.7	0%
Magnesium	78	77	78	1.7	1%
Phosphorus	0.50	0.48	0.49	0.011	4%
Potassium	7.5	7.7	7.6	0.17	3%
Silicon	12	12	12	0.27	0%
Sodium	380	380	380	8.6 -	0%
Titanium	0.046	0.045	0.046	0.0010	
nion Precursors			0.010	0.0010	_ 2%
Chloride	390	400	395	8.9	3%
Fluoride	1.8	1.9	1.9	0.042	5%
Sulfate (as SO ₄ ²)	2,800	2,800	2,800	63	
Nitrite (as N)	ND< 0.05	ND< 0.05	ND< 0.05		0%
Nitrate (as N)	0.41	0.40	0.41	ND< 0.0011 0.0091	 2%

ND<: non-detected element

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TABLE 5-24
WASTEWATER TREATMENT PLANT SAMPLE RESULTS -- WWTP OUTLET
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
SEPTEMBER 1996

Test Number	1-WWTP-O	JT 2-WWTP-OUT	AVE	RAGE	Relative
Sample Date	9/9/96	9/9/96			Percent
Sample Time	1600/2400	1600/2400			Diff.
Flow Rate, gpm	60.6	6 0.6			
pH (20°C)	7.35	7.57			
Alkalinity (as CaCO ₃), m	ng/L 17	18			
Hardness (as CaCO ₃), m	g/L 2,000	2.000			
TDS (180°C), mg/L	4,500	4.500			
TSS, mg/L	11	9.0			
Element	mg/L	mg/L	mg/L	lb/hr	
Trace Elements					
	ND< 0.033	ND< 0.033	ND< 0.033	ND< 0.0010	
•	ND< 0.0020	ND< 0.0020	ND< 0.0020	ND< 6.1E-05	
Barium	0.045	0.045	0.045	0.00136	0%
Beryllium	ND< 0.001	ND< 0.001	ND< 0.001	ND< 3.0E-05	
Cadmium	ND< 0.0001	ND< 0.0001	ND< 0.0001	ND< 3.0E-06	
Chromium	ND< 0.004	ND< 0.004	ND< 0.004	ND< 1.2E-04	
Cobalt	ND< 0.011	ND< 0.011	ND< 0.011	ND< 3.3E-04	
Copper	0.008 .	ND< 0.006	0.006	1.7E-04	91%
Lead	ND< 0.0010	ND< 0.0010	ND< 0.0010	ND< 3.0E-05	
Manganese	0.23	0.23	0.23	0.0070	0%
Mercury 1	ND< 5.0E-05	ND< 5.0E-05	ND< 5.0E-05	ND< 1.5E-06	
Molybdenum 1	ND< 0.011	ND< 0.011	ND< 0.011	ND< 3.3E-04	
Nickel 1	ND< 0.011	ND< 0.011	ND< 0.011	ND< 3.3E-04	•-
Selenium 1	ND< 0.0040	ND< 0.0040	ND< 0.0040	ND< 1.2E-04	
Vanadium 1	ND< 0.006	ND< 0.006	ND< 0.006	ND< 1.8E-04	••
Major Elements					
Aluminum	1.5	1.8	1.7	0.050	18%
Calcium	720	720	720	22	0%
Iron	0.16	0.069	0.11	0.0035	79%
Magnesium	49	49	49	1.5	0%
Phosphorus	0.18	0.17	0.18	0.0053	6%
Potassium	6.4	6.2	6.3	0.19	3%
Silicon	0.36	0.37	0.37	0.011	3%
Sodium	340	340	340	10	0%
	ND< 0.011	ND< 0.011	ND< 0.011	ND< 0.0003	••
Anion Precursors	_				
Chloride	340	350	345	10	3%
Fluoride	0.70	0.78	0.74	0.022	11%
Sulfate (as SO ₄ ²)	2,300	2,300	2,300	70	0%
	ND< 0.05	ND< 0.05	ND< 0.05	ND< 0.002	
Nitrate (as N)	0.49	0.49	0.49	0.015	0%

ND<: non-detected element

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TABLE 5-25
WASTEWATER TREATMENT PLANT SAMPLE RESULTS
COAL PILE RUN-OFF AND WWTP SLUDGE
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
SEPTEMBER 1996

Test Number	1-COALPILE	2 COAL DIT	AUEDIGE		7			
Sample Date	9/9/96	2-COALPIL 9/9/96	E AVERAGE	Relative	1		E_AVERAGE	Relativ
Sample Time	1600/240	-	00	Percent	11 71.101.70	9/10/96		Percen
Flow Rate, gpm	0	0 1600/24 0	00	Diff.	1000	1030		Diff.
Moisture, %					. NA	NA		
pH (20°C)					67	66		
	2.48	2.48				~-		
Alkalinity (as CaCC) ₃), mg/L <1.4	<1.4						
Hardness (as CaCO		2,000						
TDS (180°C), mg/L	9,700	9,600	•					
TSS, mg/L	210	260						
Element	mg/L	mg/L	mg/L		mg/Kg, dry	mg/Kg, dry	mg/Kg, dry	
Trace Elements								·
Antimony	ND< 0.033	ND< 0.033	ND = 0.022					
Arsenic	0.076	0.069	ND< 0.033		ND< 0.3	ND< 0.3	ND< 0.3	
Barium	0.021	0.069	0.073	10%	42	45	44	7%
Beryllium	0.034	0.019	0.020	10%	57	60	59	5%
Cadmium	0.016	0.033	0.034	3%	7.4	7.4	7.4	0%
Chromium	0.044		0.016	0%	3.6	3.8	3.7	5%
Cobalt	0.76	0.045	0.045	2%	23	25	24	8%
Copper		0.75	0.76	1%	150	150	150	0%
Lead	0.36	0.36	0.36	0%	91	94	93	3%
Manganese	0.0028	0.0029	0.0029	4%	4.3	6.6	5.5	42%
Mercury	11	11	11	0%	1900	1900	1900	0%
Molybdenum	ND< 5.0E-05	ND< 5.0E-05	ND< 5.0E-05	- [0.28	0.24	0.26	15%
Nickel	ND< 0.011	ND< 0.011	ND< 0.011		6.0	6.0	6.0	0%
Selenium	1.6	1.6	1.6	0%	310	310	310	0%
Vanadium	ND< 0.0040	ND< 0.011	ND< 0.0075		62	68	65	9%
	0.019	0.019	0.019	0%	24	26	25	0
fajor Elements				l l			23	U
Aluminum	150	150	150	0%	32,000	32,000	32,000	0%
Calcium	450	450	450	0%	91,000	98,000	94,500	0% 7%
Iron	650	640	645	2%	110,000	110,000	110,000	0%
Magnesium	220	220	220	0%	14,000	15,000		
Phosphorus	1.8	1.8	1.8	0%	430	470	14,500 450	7%
Potassium	5.3	4.7	5.0	12%	520	440		9%
Silicon	25 '	24	25	4%	390	440	480	17%
Sodium	600	590	595	2%	420	430 490	410	10%
Titanium	0.018	0.018	0.018	0%	120		455	15%
nion Precursors				- · · ·	120	130	125	0.08
Chloride	520	510	515	2%	440 -	470		
Fluoride	2.9	3.0	3.0	3%		470	455	7%
Sulfate (as SO ₄ ²⁻)	5,900	6.000	5,950	11	620	510	565	19%
Nitrite (as N)	ND< 0.40	1.0		2%	8,700	8,300	8,500	5%
Nitrate (as N)		ND< 0.62	0.60	133%	NA	NA		
\ ,	0.70	0.02	ND< 0.51	-	NA	NA		

ND<: non-detected element

NA -- not available

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TABLE 5-26
WASTEWATER TREATMENT PLANT RESULTS SUMMARY
NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM
SEPTEMBER 1996

			Avera	ige Sample Resu	ts		
Parameter	COALPILE,	WWT	INLET,	WWTP	OUTLET,	WWTP	WWTP Sludge
	mg/L	mg/L	lb/hr	mg/L	lb/hr	Rem. Eff.	mg/Kg, dry
Trace Elements					<u>.</u>		
Antimony	ND< 0.033	ND< 0.033	ND< 7.4E-04	ND< 0.033	ND< 0.0010	NC	ND< 0.3
Arsenic	0.073	0.022	4.8E-04	ND< 0.0020	ND< 6.1E-05	93.7%	44
Barium	0.020	0.069	0.00155	0.045	0.00136	12.2%	59
Beryllium	0.034	0.014	3.0E-04	ND< 0.001	ND< 3.0E-05	95.0%	7.4
Cadmium	0.016	0.0068	1.5E-04	ND< 0.0001	ND< 3.0E-06	99.0%	3.7
Chromium	0.045	0.034	7.5E-04	ND< 0.004	ND< 1.2E-04	92.0%	24
Cobalt	0.76	0.31	0.0070	ND< 0.011	ND< 3.3E-04	97.6%	150
Copper	0.36	0.12	0.0027	0.006	1.7E-04	93.8%	93
Lead	0.0029	0.0026	5.9E-05	ND< 0.0010	ND< 3.0E-05	74.1%	5.5
Manganese	11	4.3	0.097	0.23	0.0070	92.8%	1900
Mercury	ND< 5E-05	ND< 5E-05	ND< 1E-06	ND< 5E-05	ND< 2E-06	NC	0.26
Molybdenum	ND< 0.011	0.030	6.6E-04	ND< 0.011	ND< 3.3E-04	74.9%	6.0
Nickel	1.6	0.68	0.015	ND< 0.011	ND< 3.3E-04	98.9%	310
Selenium	ND< 0.0075	0.014	3.2E-04	ND< 0.0040	ND< 1.2E-04	80.8%	65
Vanadium	0.019	0.008	1.7E-04	ND< 0.006	ND< 1.8E-04	46.2%	25
Major Elements							
Aluminum	150	63	1.4	1.7	0.050	96.4%	32,000
Calcium	450	580	13	720	22	-67.1%	94,500
Iron	645	210	4.7	0.11	0.0035	99.9%	110,000
Magnesium	220	78	1.7	49	1.5	14.9%	14,500
Phosphorus	1.8	0.49	0.011	0.18	0.0053	51.9%	450
Potassium	5.0	7.6	0.17	6.3	0.19	-11.6%	480
Silicon	25	12	0.27	0.37	0.011	95.9%	410
Sodium	595	380	8.6	340	10	-20.4%	455
Titanium	0.018	0.046	0.0010	ND< 0.011	ND< 0.0003	83.7%	125
Anion Precursors							
Chloride	515	395	8.9	345	10	-17.5%	455
Fluoride	3.0 '	1.9	0.042	0.74	0.022	46.2%	565
Sulfate (as SO ₄ ²)	5,950 _	2,800	63	2,300	70	-10.5%	8,500
Nitrite (as N)	0.60	ND< 0.05	ND< 0.0011	ND< 0.05	ND< 0.002	NC	
Nitrate (as N)	ND< 0.51	0.41	0.0091	0.49	0.015	-62.8%	
		IS .					II:

ND<: non-detected element

NC: not calculable using non-detected results.



coal pile is a major source of them entering the WWTP, and that a majority of them end up in the sludge for disposal.

• WWTP removal efficiencies of around 75% or greater were seen for most target inorganic elements detected in the WWTP inlet stream. The treatment plant exhibited low removals for barium (12%), vanadium (46%), phosphorus (52%), and fluoride (46%). Negative or very low removals were seen for many of the water soluble elements (i.e. Ca, Mg, K, Na, Cl, S, N) suggesting that another input stream to the WWTP was a significant source of these elements, such as chemical treatment additives (e.g. lime and ferric chloride).

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SECTION 6.0

MERCURY SPECIATION FLUE GAS TEST RESULTS

This section presents the results of flue gas tests performed to collect and quantify species of mercury as part of the post-retrofit Unit 2 test program. More detailed results including laboratory analyses can be found in Appendix C. Boiler/ESP and FGD mass balance results for total mercury as measured from the EPA Method 29 sample train were presented in Section 5.0. For this section, total mercury levels determined in the solids and liquid/sludge sample streams are combined with each set of flue gas mercury test results to calculate their individual material balances as a quality assurance measure.

The objective of performing these mercury speciation sampling methods at the Milliken Station was to evaluate and compare their performances at measuring mercury species on a fullscale, utility basis. This program did not attempt to evaluate all mercury speciation methods currently in development. From previous developmental work, the Ontario-Hydro and TRIS Buffer techniques have shown significant promise, whereas EPA Method 29 and Frontier Geosciences have produced questionable mercury speciation results. All four methods, however, have generally agreed on total mercury.

6.1 COMPARISON OF AVERAGE FLUE GAS MERCURY SPECIATION RESULTS

The Milliken Unit 2 mercury speciation results generally agree with previous EPRI and DOE sponsored research findings, namely:

- 1) EPA Method 29, Frontier Geoscience, Ontario-Hydro, and TRIS Buffer provide comparable total mercury results.
- 2) Ontario-Hydro and TRIS Buffer provide similar mercury speciation results. Given the agreement between these methods, and their success during bench- and pilotscale evaluation programs, they are considered the "benchmarks" for mercury speciation method comparisons.
- 3) EPA Method 29 and Frontier Geoscience results suffer from biases associated with flue gas SO₂ and NO₃ (Frontier Geoscience only) levels.



TABLE 6-1 SUMMARY OF MERCURY SPECIATION TEST RESULTS NYSEG MILLIKEN UNIT 2 POST-RETROFIT TEST PROGRAM **AUGUST 1996**

Mercury Specie	s Test Method	Emi	ssion Results, u	g/Nm ³	ESP Removal	FGD Remove
		ESP Inlet	ESP Outlet/ FGD Inlet	FGD Outlet/ Stack	Efficiency ⁽¹⁾	Efficiency ⁽¹⁾
Hg(0) - Elementa	<u>.l</u>					
	EPA Method 29	0.80	1.49	2.40		
•	Frontier Geoscience	2.12	2.66	2.40 2.94		
	Ontario-Hydro		2.28	2.45		
	TRIS Buffer		2.70	2.43		
	Semtech Hg 2000 Analyzer ⁽²⁾					
	2000 1 2141,7201	_	NV	2.61		
Hg(II) - Oxidized						
	EPA Method 29	7.43	6.23	0.62	18%	
	Frontier Geoscience	6.93	6.82	0.35	18% 5%	90%
	Ontario-Hydro		5.24	0.33	3%	95%
	TRIS Buffer		4.46	0.21	**	96%
			0	0.15		97%
Ig(total) - Hg Sol	<u>ids</u>					
	EPA Method 29	0.86	ND<0.009	0.006	99.5%	
	Frontier Geoscience ⁽³⁾	0.06	0.07	0.003	77.376	
	Ontario-Hydro		0.0003	0.003		
	TRIS Buffer		0.002	0.0009	-	-
			0.002	0.004	-	-
OTAL Hg ⁽⁴⁾						
	EPA Method 29	9.09	7.72	3.02	17%	600 4
	Frontier Geoscience	9.11	9.56	3.29	1/70	60%
	Ontario-Hydro	••	7.52	2.66		65%
	TRIS Buffer		7.16	2.87		64%
			7.10	4.07		59%

NV -- results not valid. Semtech analyzer measurements performed at this location were deemed invalid due to the use of an improper sample conditioning system and detrimental ambient conditions (i.e. high temperature and dust level).

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⁽¹⁾ Removal efficiencies calculated using emission units of lb/10¹²Btu to account for any differences in flue gas dilution between locations.

⁽²⁾ The Semtech Hg 2000 analyzer only measures elemental mercury.

⁽³⁾ The Frontier Geoscience method is not designed to representatively quantify the mercury solids fraction. These values represent mercury vapor that adsorbed on the flyash collected on the quartz wool plug during sampling.

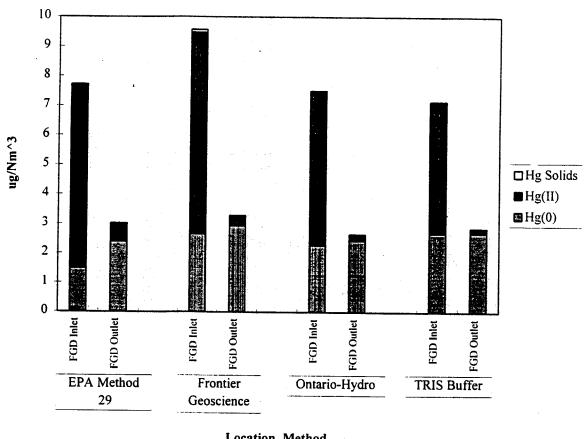
⁽⁴⁾ Total Hg is the sum of Hg(0), Hg(II), and Hg solids.

TABLE 6-1A
PARTITIONING OF MERCURY SPECIES BY METHOD
NYSEG POST-RETROFIT TEST PROGRAM -- UNIT 2
AUGUST 1996

Test Method	ESP Outlet	/FGD Inlet	FGD Ou	tlet/Stack
	Hg(0)	Hg(II)	Hg(0)	Hg(II)
EPA Method 29	19%	81%	79%	21%
Frontier Geoscience	28%	71%	89%	11%
Ontario-Hydro	30%	70%	92%	8%
TRIS Buffer	38%	62%	94%	6%







Location, Method

Figure 6-1. FGD Inlet vs. FGD Outlet Mercury Levels

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Table 6-1 provides a summary that compares each set of average mercury speciation test results including EPA Method 29. Table 6-1A shows the average percent split of mercury species found at the ESP outlet/FGD inlet and FGD outlet/stack. Figure 6-1 illustrates ESP outlet/FGD inlet verses FGD outlet/stack mercury levels as measured by each method. Table 6-2A and Table 6-2B present the mass balance results. Listed below are the key observations made in regards to this data set. Excellent agreement between a set of results is defined as differences less than 0.6 ug/Nm³, and good agreement would be differences on the order of 0.6 to 1.0 ug/Nm³. As a reminder, the Semtech Hg 2000 analyzer only measures elemental mercury.

EPA Method 29

- In comparison with the Ontario-Hydro and TRIS Buffer results, the EPA Method 29 mercury speciation values obtained from this test program exhibit a high bias for Hg(II), and a low bias for Hg(0). This bias occurs when flue gas SO₂ collects in the nitric acid/peroxide impingers producing a solution that will oxidize a portion of the Hg(0) as it passes through these impingers. The amount of oxidation that occurs appears to be proportional to the amount of flue gas SO₂.
- Coal flyash has been shown to oxidize Hg(0) to Hg(II) at typical flue gas conditions in bench- and pilot-scale evaluation programs. It is expected, therefore, that flyash trapped on a "Method 29-style" sampling filter would oxidize Hg(0) as it passes through it. Only at the ESP inlet using EPA Method 29 did an appreciable amount of flyash collect on the sampling filter. At this location the Hg(0) was biased even lower (and Hg(II) biased even higher) than at the ESP outlet/FGD inlet, suggesting that the oxidizing capacity of the flyash trapped on the filter and the SO₂ trapped in the nitric acid/peroxide impingers is additive.

Frontier Geoscience

- The Frontier Geoscience method reported Hg(II) levels for the ESP outlet/FGD inlet that were 1.6-2.3 ug/Nm³ higher than the average results from Ontario-Hydro and TRIS. Bench- and pilot-scale evaluations of the Frontier Geoscience method uncovered a high bias associated with its measurement of Hg(II). This high bias occurs when the flue gas contains high levels of SO₂ (around 1500 ppm or higher) in the presence of NO_x, which will oxidize in the soda lime traps to form NO₂. A reaction then occurs between NO₂ and Hg(0) to form Hg(II). This would mean, however, that Frontier's Hg(0) results should be biased low, which does not appear to be the case.
- The Frontier Geoscience and EPA Method 29 results for the ESP inlet location agreed at 6.9-7.0 lb/10¹²Btu which amounts to approximately 94% of the total

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TABLE 6-2A
SUMMARY OF TOTAL MERCURY MASS BALANCE RESULTS -- BOILER/ESP
NYSEG POST-RETROFIT TEST PROGRAM -- UNIT 2
AUGUST 1996

Test Method		Mass B	alance Results, lb/	'10 ¹² Btu	•		
	Coal	ESP Inlet	Bottom Ash	Fly Ash	ESP Outlet/ FGD Inlet	Boiler/ESP Mass Balance ⁽¹⁾	ESP Mass Balance ⁽²⁾
Frontier Geosciences Ontario-Hydro TRIS Buffer	7.4	6.97 NP NP	-0.01	0.57	7.04 5.58 5.22	103% 83% 78%	109%
EPA Method 29		6.89			5.74	85%	91%

Notes:

TABLE 6-2B
SUMMARY OF TOTAL MERCURY MASS BALANCE RESULTS -- FGD
NYSEG POST-RETROFIT TEST PROGRAM -- UNIT 2
AUGUST 1996

Test Method		Mass Ba	alance Results, lb/	10 ¹² Btu		
	IN	PUTS		OUTPUTS	·	FGD
	ESP Outlet/ FGD Inlet	Limestone	FGD Sludge	Gypsum	FGD Outlet/ Stack	Mass Balance (Outputs/Inputs)
Frantis Court		0.04	0.31	2.76		
Frontier Geosciences					2.49	79%
Ontario-Hydro	5.58				2.01	90%
TRIS Buffer	5.22	•			2.14	99%
EPA Method 29	5.74				2.31	93%

Note: No mercury was detected in FGD liquid streams.

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⁽¹⁾ Boiler/ESP Mass Balance, Output/Input = (Bottom Ash + Flyash + ESP Outlet)/Coal

⁽²⁾ Mass Balance, ESP = (Flyash + ESP Outlet)/ESP Inlet

mercury found in the coal. ESP inlet results from these two methods are not expected to agree, however, because Frontier's sampling method is not designed to measure the additional 10% of total mercury adsorbed on the flyash as found in the Method 29 sample trains. This suggests that the Frontier Geoscience ESP inlet results may be biased high by at least 10%.

EPA Method 29, Frontier Geoscience, Ontario-Hydro, and Tris Buffer

- For the FGD outlet/stack location, excellent agreement between the Frontier Geoscience, Ontario-Hydro and TRIS Buffer measurements can be seen for Hg(0) and Hg(II). Hg(0) results ranged from 2.45-2.94 ug/Nm³ (excluding Method 29) and Hg(II) results ranged from 0.15-0.35 ug/Nm³ (excluding Method 29). Good to excellent agreement exists between Frontier, Ontario-Hydro, TRIS and EPA Method 29 for total mercury with results ranging from 2.66-3.29 ug/Nm³.
- For the ESP outlet/FGD inlet, excellent agreement between Frontier, Ontario-Hydro, and TRIS can be seen for Hg(0) with levels ranging from 2.28-2.70 ug/Nm³.
- For the ESP outlet/FGD inlet, Ontario-Hydro and TRIS Buffer values are in good agreement for Hg(II); and Ontario-Hydro, TRIS and EPA Method 29 are in excellent agreement for total mercury.
- The partitioning of mercury between Hg(0) and Hg(II) at the ESP outlet/FGD inlet finds 28-38% as Hg(0) and 62-71% as Hg(II). At the FGD outlet/stack, 89-94% of the mercury was measured as Hg(0) with the remaining percentage as Hg(II). Method 29's high bias in measuring Hg(II) amounts to 10-20% at the ESP outlet/FGD inlet and 10-15% at the FGD outlet/stack. For the ESP outlet/FGD inlet, the Ontario-Hydro partitioning results show a 30/70 split between Hg(0) and Hg(II), whereas the TRIS results show almost a 40/60 split. Since total mercury as measured by both methods agree, there appears to be a small bias of some sort associated with one or both of the method's speciation capabilities. The 6 hour sampling time used for the Ontario-Hydro method verses 1-2 hours for TRIS may be a contributing factor.

Semtech HG 2000 Analyzer

• There is excellent agreement between the average FGD outlet/stack Hg(0) result as measured by the Semtech mercury analyzer with the other valid measurements at that location.

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ESP/FGD Removal Efficiencies

- Apparent ESP/FGD removal efficiencies for Hg(II) as measured by the EPA
 Method 29 sample train are not valid; rather an artifact of decreasing levels of
 Hg(0) oxidation.
- The ESP was effective at removing mercury adsorbed on the flyash at a rate of 99.5%. Mercury solids accounted for nearly 10% of total mercury levels found at the ESP inlet, resulting in an overall total mercury ESP removal efficiency of 17% as measured by EPA Method 29.
- FGD removal efficiencies were between 95-97% for Hg(II) (excluding EPA Method 29) and 59-65% for total mercury.

Mass Balance Results

- Boiler/ESP mass balance results using Frontier Geoscience, Ontario-Hydro, TRIS Buffer, and EPA Method 29 total mercury values yielded 103%, 83%, 78%, and 85% agreement, respectively, between process streams.
- Total mercury FGD mass balance results for Frontier Geoscience, Ontario-Hydro, TRIS Buffer, and EPA Method 29 were 79%, 90%, 99%, and 93%, respectively.
- Excellent FGD mass balance results for the wet chemical mercury speciation methods, and the agreement between all FGD outlet values including Frontier's suggests that the Frontier Geoscience ESP outlet/FGD inlet mercury level is biased high by 20%.
- Coal mercury levels appear to be biased high by 7-15% based on the EPA Method 29 ESP inlet measurements, the excellent agreement among wet chemical mercury data at the ESP outlet/FGD inlet, and their FGD mass balance results.
- An ESP mass balance for the Frontier Geoscience method was 109%. A 9-10% high bias in this balance is expected since the Frontier Geoscience results for the ESP inlet do not include any mercury adsorbed on the flyash.

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DAILY COMPARISONS OF MERCURY SPECIATION RESULTS **NYSEG POST-RETROFIT TEST PROGRAM -- UNIT 2** AUGUST 1996 TABLE 6-3

To the second se								
	Test 1	Test 1, 8/7/96	Test 2	Test 2, 8/8/96	Test 3,	Test 3, 8/9/96	Ave	Average
	FGD Inlet	FGD Inlet FGD Outlet	FGD Inlet	FGD Inlet FGD Outlet	FGD Inlet	FGD Inlet FGD Outlet	FGD Inlet	FGD Inlet FGD Outlet
		1						,
Hg(0) - Elemental								
EPA Method 29	1.06	2.27	1.66	2.69	1.75	2.23	1.49	2.40
Frontier Geoscience	Ω¥Χ	2.79	1.49	2.88	$3.25^{(3)}$	$3.05^{(3)}$	2.66	2.94
Ontario-Hydro	2.00	2.33	2.25	2.35	2.60	2.68	2.28	2.45
TRIS Buffer	2.17	2.51	5.69	2.90	3.24	2.73	2.70	17.7
Semtech Hg 2000 Analyzer	₽	2.17	ď	3.03	NA ⁽²⁾	2.63	N A	2.61
Hg(II) - Oxidized								
EPA Method 29	5.85	0.46	7.21	0.56	5.63	0.82	6.23	19.0
Ontario-Hydro	5.25	0.31	5.59	0.16	4.88	0.16	5.24	0.21
Frontier Geoscience	NAC	0.27	8.37	0.40	$6.05^{(3)}$	$0.36^{(3)}$	6.82	0.35
TRIS Buffer	4.64	0.18	4.71	0.23	4.03	0.03	4.46	0.15
TOTAL He								
EPA Method 29	6.92	2.74	8.86	3.25	7.38	3.07	7.72	3.02
Frontier Geoscience	NAE	3.06	9.87	3.29	$9.37^{(3)}$	$3.41^{(3)}$	9.56	3.29
Ontario-Hydro	7.25	2.63	7.84	2.51	7.48	2.84	7.52	2.66
TRIS Buffer	6.81	2.69	7.40	3.14	7.27	2.76	7.16	2.87

NP -- test not performed NA -- data not available

(1) Test run invalid, mercury levels reported by the laboratory were similar to those found in trip blanks. Test may not have sampled flue gas due to an undetected leak in sample train.

(2) Semtech analyzer measurements performed at this location were deemed invalid due to the use of an improper sample conditioning system and detrimental ambient conditions (i.e. high temperature and dust level). Please see Section 3.1.11 for further discussion.

(3) Results presented are an average of two sample runs performed on this day.

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6.2 COMPARISON OF DAILY FLUE GAS MERCURY SPECIATION RESULTS

Daily comparisons of mercury speciation results generated by each method are presented in Table 6-3 and illustrated in Figure 6-2 and Figure 6-3. Throughout the inorganic test period, operation of the boiler and ESP/FGD control devices was steady within acceptable tolerances and not considered a contributing factor to any day to day fluctuations in mercury speciation results. In general, mercury speciation results for each method are consistent from day to day.

Examining the Ontario-Hydro and TRIS Buffer results more closely reveals a consistent yet minor difference between the methods. For both locations, Hg(0) levels reported by the Ontario-Hydro method were consistently lower (between 0.1-0.6 ug/Nm³) than the TRIS Buffer values suggesting the existence of a small bias in one or both method's measurement technique as mentioned in Section 6.1.

6.3 DETAILED MERCURY SPECIATION METHOD RESULTS

The following tables present detailed mercury speciation test results for each method:

Table 6-4:	EPA Method 29	Mercury	Emission	Results	ESP	Inlet
------------	---------------	---------	----------	---------	-----	-------

Table 6-5: EPA Method 29 Mercury Emission Results -- ESP Outlet/FGD Inlet

Table 6-6: EPA Method 29 Mercury Emission Results -- FGD Outlet/Stack

Table 6-7: Frontier Geoscience Mercury Speciation Test Results -- ESP Inlet

Table 6-8: Frontier Geoscience Mercury Speciation Test Results -- ESP Outlet/FGD

Table 6-9: Frontier Geoscience Mercury Speciation Test Results -- FGD Outlet/Stack

Table 6-10: TRIS Buffer and Ontario-Hydro Mercury Speciation Test Results -- ESP Outlet/FGD Inlet

Table 6-11: TRIS Buffer and Ontario-Hydro Mercury Speciation Test Results -- FGD Outlet/Stack

Table 6-12: Semtech Hg 2000 Analyzer Test Results

For almost all sets of valid mercury speciation measurements, agreement between individual replicates for the EPA Method 29, Frontier Geoscience, Ontario-Hydro, and TRIS Buffer methods were excellent (95% CI uncertainties of less than 50%) when concentration levels were measured above 0.5 ug/Nm³. Poor agreement (uncertainties above 150%) between Frontier Geoscience replicate results for Hg(0) at the ESP inlet and ESP outlet/FGD inlet locations was seen, which could be due to the high SO₂ levels.

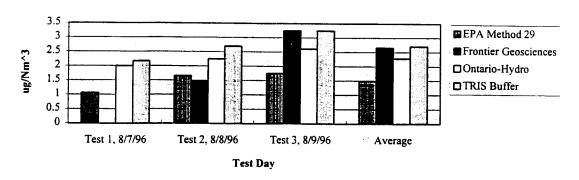
As mentioned in Section 6.1, the Frontier Geoscience method does not quantify the mercury solids fraction. Total mercury found on the quartz wool plug represents mercury vapor

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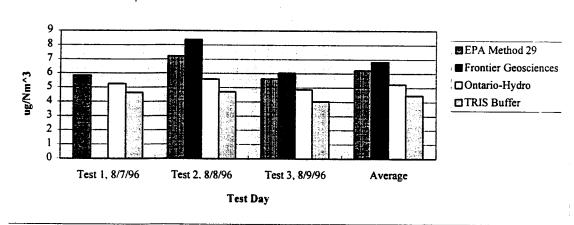
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Hg(0) - Elemental, FGD INLET



Hg(II) - Oxidized, FGD INLET



Total Hg, FGD INLET

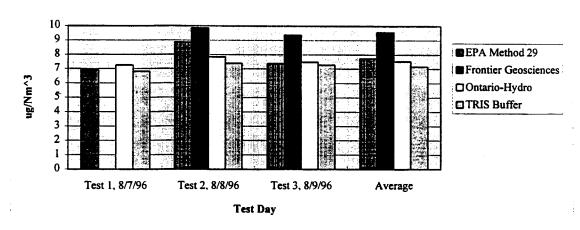
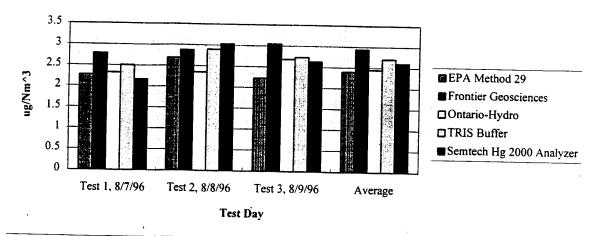
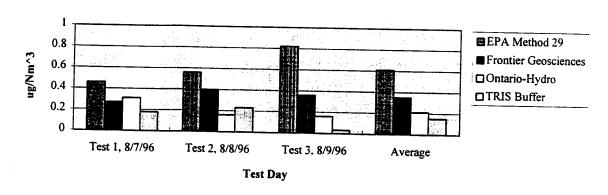


Figure 6-2. Comparison of Daily Mercury Speciation Method Results for FGD Inlet

Hg(0) - Elemental, FGD OUTLET



Hg(II) - Oxidized, FGD OUTLET



Total Hg, FGD OUTLET

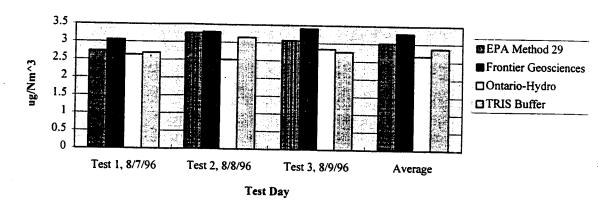


Figure 6-3. Comparison of Daily Mercury Speciation Method Results for FGD Outlet

TABLE 6-4
EPA METHOD 29 MERCURY EMISSION RESULTS
NYSEG POST-RETROFIT TEST PROGRAM -- ESP INLET
AUGUST 1996

Test Number	1-MTLS-IN	2-MTLS-IN	3-MTLS-IN	F	VERAG	Ē	Und	ertainty
Date	8/7/96	8/8/96	8/9/96				_	95%CI
Pitot Flow Rate, dscfm	325,318	340,247	327,659					
Sample Volume, dscf	137.91	144.70	135.15					
Fuel Factor, dscf/106Btu	13,106	12,740	13,355					
O ₂ , %	5.60	5.10	5.79					
CO ₂ , %	13.86	13.94	13.64					
H ₂ O, %	8.5	8.7	8.5					
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Bt	u	ug/Nm
Hg(0) - elemental	0.80	0.76	0.84	0.80	0.001	0.61	13%	0.10
Hg(II) - oxidized	7.33	8.14	6.81	7.43	0.009	5.63	22%	1.67
Hg(total) - front 1/2 solid	0.93	0.99	0.66	0.86	0.001	0.65	50%	0.43
Total Hg	9.05	9.89	8.32	9.09	0.011	6.89	21%	1.95

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TABLE 6-5 EPA METHOD 29 MERCURY EMISSION RESULTS NYSEG POST-RETROFIT TEST PROGRAM -- ESP OUTLET/FGD INLET **AUGUST 1996**

Test Number Date	1-MTLS-OUT 8/7/96	2-MTLS-OUT 8/8/96		Γ	AVERAGE		Un	certainty
Pitot Flow Rate, dscfm Sample Volume, dscf Fuel Factor, dscf/10 ⁶ Btu O ₂ , % CO ₂ , % H ₂ O, %	323,354 221.74 12,920 5.38 14.06 8.3		8/9/96 330,081 216.78 12,723 5.04 14.32 8.1				-	95%CI
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm ³	lb/hr	Ib/10 ¹² Btu		ug/Nm
Hg(0) - elemental Hg(II) - oxidized Hg(total) - front 1/2 solids	1.06 5.85 ND< 0.02	1.66 7.21 ND< 0.005	1.75 5.63 ND< 0.005	1.49 6.23 ND< 0.009	0.002 0.007 ND< 9.8E-06	1.10 4.63 ND< 0.006	62% 34%	0.93

	ug/Nm	ug/Nm ³	ug/Nm ³	ug/Nm	lb/hr	Ib/10 ¹² Btu		ug/Nm ³
Hg(0) - elemental Hg(II) - oxidized Hg(total) - front 1/2 solids	1.06 5.85 ND< 0.02	1.66 7.21 ND< 0.005	1.75 5.63 ND< 0.005	1.49 6.23 ND< 0.009	0.002 0.007 ND< 9.8E-06	1.10 4.63 ND< 0.006	62% 34%	0.93
Total Hg	6.92	8.86	7.38	7.72	0.009	5.74	33%	2.52

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TABLE 6-6
EPA METHOD 29 MERCURY EMISSION RESULTS
NYSEG POST-RETROFIT TEST PROGRAM -- FGD OUTLET/STACK
AUGUST 1996

Test Number	1-MTLS-STK	2-MTLS-STK	3-MTLS-STK	Δ	VERAGE		Unc	ertainty
Date	8/7/96	8/8/96	8/9/96				- @9	95%CI
Pitot Flow Rate, dscfm	358.667	358,779	362,692					
Sample Volume, dscf	241.79	253.28	254.55					
Fuel Factor, dscf/106Btu	13,157	13,088	13.328					
O ₂ , %	5.66	5.52	5.76					
CO ₂ , %	13.81	13.57	13.67					
H ₂ O, %	14.4	14.8	14.3					
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² B	tu	ug/Nm
Hg(0) - elemental	2.27	2.69	2.23	2.40	0.003	1.84	26%	0.63
Hg(II) - oxidized	0.46	0.56	0.82	0.61	0.001	0.47	75%	0.46
Hg(total) - front 1/2 solids	ND< 0.005	ND< 0.004	0.015	0.006	8.2E-06	0.005	~~	
Total Hg	2.74	3.25	3.07	3.02	0.004	2.31	21%	0.65



TABLE 6-7 FRONTIER GEOSCIENCE MERCURY SPECIATION TEST RESULTS NYSEG POST-RETROFIT TEST PROGRAM -- ESP INLET **AUGUST 1996**

12.93	13.64	13.75			
6:13	5.40	5.23			
13,628	13,019	12.877			
1.64	1.71	1.97			
340,247			AVERAG	<u>E</u>	@95%CI
					Uncertainty
	1.64 13,628	8/8/96 8/9/96 340,247 327,659 1.64 1.71 13,628 13,019 6.13 5.40	8/8/96 8/9/96 8/9/96 340,247 327,659 329,486 1.64 1.71 1.97 13,628 13,019 12.877 6.13 5.40 5.23	8/8/96 8/9/96 8/9/96 AVERAG 340,247 327,659 329,486 1.64 1.71 1.97 13,628 13,019 12,877	8/8/96 8/9/96 8/9/96 AVERAGE 340,247 327,659 329,486 1.64 1.71 1.97 13,628 13,019 12.877 6.13 5.40 5.23

Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu		ug/Nm ³
Hg(0) - elemental Hg(II) - oxidized Hg(tot) - Quartz Wool Plug*	1.62 7.03 0.08	3.75 6.15 0.08	0.98 7.62 0.01	2.12 6.93 0.06	0.002 0.008 6.7E-05	1.62 5.31 0.04	170% 26% 186%	3.59 1.83 0.11
Total Hg	8.74	9.98	8.61	9.11	0.011	6.97	21%	1.87

^{*}Frontier Geoscience method is not designed to representatively quantify the mercury solids fraction, these values represent mercury vapor that adsorbed on the flyash collected on the quartz wool plug during sampling.

Note: The sample from test 1-MESA-IN performed on 8/7/96 was lost after the test was completed.

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TABLE 6-8 FRONTIER GEOSCIENCE MERCURY SPECIATION TEST RESULTS NYSEG POST-RETROFIT TEST PROGRAM -- ESP OUTLET/FGD INLET **AUGUST 1996**

Test Number	2-MESA-OUT	3-MESA-OUT	3A-MESA-O	ÚŤ			Line	anta in tr
Date	8/8/96	8/9/96	8/9/96		AVERAC	3F		ertainty
Pitot Flow Rate, dscfm	331,647	330,081	330.081		TIVEIGIC	<u> </u>	<u>u</u>	95%CI
Sample Volume, dscf	2.77	2.78	2.76					
Fuel Factor, dscf/106Btu	12,936	12,952	12,119					
O ₂ , %	5.34	5.32	4.25					
CO ₂ ,%	13.62	13.71	14.61					
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	ib/10 ¹² Btu		ug/Nm³
Hg(0) - elemental	1.49	2.04	4.47	2.66	0.003	1.02	1.400/	
Hg(II) - oxidized	8.37	7.05	5.06	6.82		1.93	148%	3.94
Hg(tot) - Quartz Wool Plug*	0.01	0.14	ND	0.07	0.008 8.4E-05	5.05 0.06	61% 264%	4.14 0.19
Total Hg	9.87	9.22	9,52	9.56	0.011	7.04	8%	0.80

ND -- mercury not detected in sample fraction above trip blank level (treated as zero).

Note: Test 1-MESA-OUT performed on 8/7/96 was deemed invalid, mercury levels reported by the laboratory were similar to those found in trip blanks. Test may not have sampled flue gas due to an undetected leak in sample train.



^{*}Frontier Geoscience method is not designed to representatively quantify the mercury solids fraction, these values represent mercury vapor that adsorbed on the flyash collected on the quartz wool plug during sampling.

TABLE 6-9
FRONTIER GEOSCIENCE MERCURY SPECIATION TEST RESULTS
NYSEG POST-RETROFIT TEST PROGRAM -- FGD OUTLET/STACK
AUGUST 1996

Date	1-MESA-STK 8/7/96	2-MESA-STK 8/8/96	3-MESA-STK 8/9/96	3A-MESA-ST) 8/9/96	K	AVERAC	F.		ertainty
Pitot Flow Rate, dscfm Sample Volume, dscf	358,667 1.80	358.779 1.67	362.692 3.23	362,692 2.86		- TTV ETG TG	<u> </u>		95%CI
Fuel Factor, dscf/10 ⁶ Btu O ₂ , %	13.131 5.63	12,928 5.33	12,977 5.35	12.960					
CO ₂ ,%	13.86	13.63	13.68	5.33 13.66					
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu		ug/Nm
Ig(0) - elemental Ig(II) - oxidized Ig(tot) - Quartz Wool Plug	2.79 0.27 NP	2.88 0.40 0.003	3.19 0.45 0.003	2.91 0.27 0.001	2.94 0.35 0.003	0.004 0.0004 3.3E-06	2.22 0.26 0.002	9% 42% 121%	0.27 0.15 0.00
otal Hg	3.06	3.29	3.64	3.18	3.29	0.004	2.49	12%	0.39

NP -- analysis not performed



^{*}Frontier Geoscience method is not designed to representatively quantify the mercury solids fraction, these values represent mercury vapor that adsorbed on the flyash collected on the quartz wool plug during sampling.

TABLE 6-10
ONTARIO-HYDRO AND TRIS BUFFER MERCURY SPECIATION TEST RESULTS
NYSEG POST RETROFIT TEST PROGRAM -- ESP OUTLET/FGD INLET
AUGUST 1996

			ONTAI	UO-HYDI	RO	<u> </u>		
Test Number	1-ONT-OUT	2-ONT-OUT	3-ONT-OUT		AVERAGI	E	Unc	ertainty
Date	8/7/96	8/8/96	8/9/96				@9	5%CI
Pitot Flow Rate, dscfm	323,354	331,647	330,081					
Sample Volume, dscf	261.06	224.41	209.72					
Fuel Factor, dscf/106Btu	12,532	12,837	12,739					
O ₂ , %	4.90	5.28	5.16					
CO ₂ ,%	14.47	13.63	13.83					
Parameter	ug/Nm³	ug/Nm ³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu		ug/Nm³
Hg(0) - elemental	2.00	2.25	2.60	2.28	0.003	1.69	33%	0.75
Hg(II) - oxidized	5.25	5.59	4.88	5.24	0.006	3.88	17%	0.87
Hg(tot) - filter	ND	0.0008	ND	0.0003	3.3E-07	0.0002		
Hg (total)	7.25	7.84	7.48	7.52	0.009	5.58	10%	0.73
				BUFFER				
		2-TRIS-OUT			AVERAGE	3	Unc	ertainty
Date	8/7/96	8/8/96	8/9/96				@9	5%CI
Pitot Flow Rate, dscfm	323,354	331,647	330,081					
Sample Volume, dscf	35.83	39.46	39.22					
Fuel Factor, dscf/10 ⁶ Btu	12,355	12,821	12,433	·				
O ₂ , %	4.67	5.20	4.67					
CO ₂ ,%	14.56	13.44	14.13					
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu		ug/Nm ³
Ua(0) elemental	2.17	2.60	2.24	2.70	0.002	1.07	400/	1 22
Hg(0) - elemental Hg(II) - oxidized	- 2.17 4.64	2.69 4.71	3.24	2.70	0.003	1.97	49%	1.33
ng(11) - oxidized Hg(tot) - filter	0.001	0.006	4.03 ND	4.46 0.002	0.005°	3.25	21%	0.92
ng(w) - mer	0.001	0.000	עא	0.002	2.6E-06	0.002		
Hg (total)	6.81	7.40	7.27	7.16	0.008	5.22	11%	0.77

ND -- mercury not detected in fraction (treated as zero).



TABLE 6-11 ONTARIO-HYDRO AND TRIS BUFFER MERCURY SPECIATION TEST RESULTS NYSEG POST RETROFIT TEST PROGRAM -- FGD OUTLET/STACK AUGUST 1996

_			ONTA	ONTARIO-HYDRO							
Test Number	I-ONT-STK	2-ONT-STK	3-ONT-STK	· · · · · · · · · · · · · · · · · · ·	AVERAC	GE	Lin	ertainty			
Date	8/7/96	8/8/96	8/9/96					95%CI			
Pitot Flow Rate, dscfm	358,667	358,779	362,692				<u>u</u>	73 /0C1			
Sample Volume, dscf	215.77	224.11	225.28								
Fuel Factor, dscf/106Btu	13,114	12,862	12,870					ş - ⁷			
O ₂ , %	5.61	5.31	5.32								
CO ₂ ,%	13.83	13.60	13.69								
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm³	lb/hr	lb/10 ¹² Btu		ug/Nm³			
						15/10 Btu		ug/iviii			
Hg(0) - elemental	2.33	2.35	2.68	2.45	0.003	1.85	20%	0.50			
Hg(II) - oxidized	0.31	0.16	0.16	0.21	0.0003	0.16	101%	0.30			
Hg(tot) - filter	ND	0.0010	0.0017	0.0009	1.1E-06	0.0007					
Hg (total)	2.63	2.51	2.84	2.66	0.003	2.01	15%	0.41			
F-43V				S BUFFE	₹						
			3-TRIS-STK		AVERAG	E	Unc	rtainty			
Date	8/7/96	8/8/96	8/9/96					5%CI			
Pitot Flow Rate, dscfm	358.667	358.779	362,692								
Sample Volume, dscf	71.83	73.71	73.58		•						
Fuel Factor, dscf/106Btu	12,953	12.780	12,877								
02, %	5.42	5.15	5.23								
CO ₂ ,%	13.89	13.48	13.64								
Parameter	ug/Nm³	ug/Nm³	ug/Nm³	ug/Nm ³	lb/hr	lb/10 ¹² Btu	-	ug/Nm³			
Ig(0) - elemental	2.51	2.00									
Ig(II) - oxidized	2.51 0.18	2.90	2.73	2.71	0.003	2.03	18%	0.50			
Ig(tot) - filter		0.23	0.03	0.15	0.0002	0.11	175%	0.26			
eg(tot) • Hitter	0.005	0.003	0.004	0.004	4.8E-06	0.003	190%	0.00			
Ig (total)	2.69	3.14	2.76	2.87	0.004	2.14	21%	0.59			

ND -- mercury not detected in fraction (treated as zero).

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TABLE 6-12 SEMTECH HG 2000 ANALYZER TEST RESULTS NYSEG POST-RETROFIT TEST PROGRAM -- UNIT 2 **AUGUST 1996**

	Semte	ch Hg Analyzer F	Results
_	Ontario-Hydro	TRIS Buffer	Average*
Parameter	Test Period	Test Period	•
T- / 1 0/2/07			
Test 1, 8/7/96			
Hg(0) - Elemental, ug/dscm	1.86	2.50	2.02
Hg(0) - Elemental, ug/Nm ³	2.00	2.68	2.17
Test 2, 8/8/96			
Hg(0) - Elemental, ug/dscm	2.73	3.08	2.82
Hg(0) - Elemental, ug/Nm ³	2.93	3.31	3.02
Test 3, 8/9/96			
Hg(0) - Elemental, ug/dscm	2.45	NA	2.45
Hg(0) - Elemental, ug/Nm ³	2.63		2.63
Averages			
Hg(0) - Elemental, ug/dscm	2.35	2.79	2.43
Hg(0) - Elemental, ug/Nm ³	2.52	2.99	2.61

NA -- data not available for this test period.



^{*}Represents a weighted average that is based on test period durations.

that adsorbed on the flyash collected on the wool plug during sampling. Given the flyash mercury concentration level, the small amount of flyash collected on the wool plug does not represent any significant level of mercury solids.

Figures 6-4, 6-5, and 6-6 present the daily data trend charts for the Semtech analyzer's operation during the inorganic test period for Ontario-Hydro and TRIS sampling periods. As shown on each figure, there is excellent agreement between the Semtech analyzer's Hg(0) output levels and those for the wet chemical techniques. For Test 1 on 8/7/96, Hg(0) Semtech results averaged 2.2 ug/m³ but ranged between 1 and 5 ug/m³. For Test 2, Semtech results averaged 2.9 ug/m³ but only ranged between 1.5 and 4 ug/Nm³; and for Test 3 average results were 2.5 ug/m³ and the range was 1.5 to 3.5 ug/Nm³.

6.4 MERCURY SPECIATION METHODS QUALITY ASSURANCE/QUALITY CONTROL DATA

Tables 6-13, 6-14, 6-15, 6-15A present the quality assurance/quality control results for EPA Method 29, Frontier Geoscience, Ontario-Hydro, and TRIS Buffer test methods.

Matrix spike recoveries were all between 85-120%. No significant levels of mercury were found in any of the method's trip, reagent or field blanks. Distribution of mercury throughout the ESP outlet/FGD inlet Ontario-Hydro and TRIS Buffer sample trains found 17-19% of the total mercury in the probe rinses. As discussed in Section 3.2.4, probe rinse mercury was counted as Hg(II).

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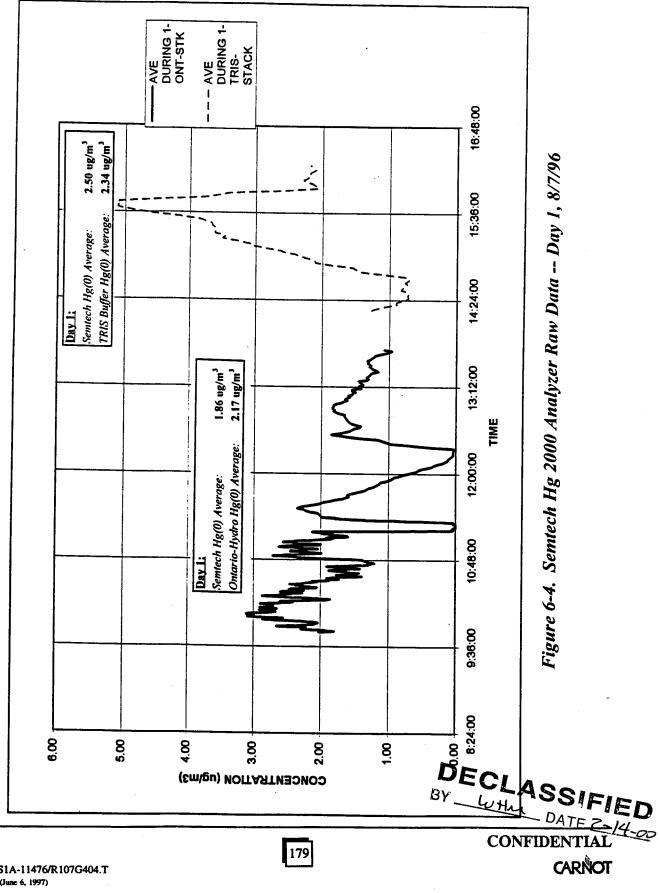
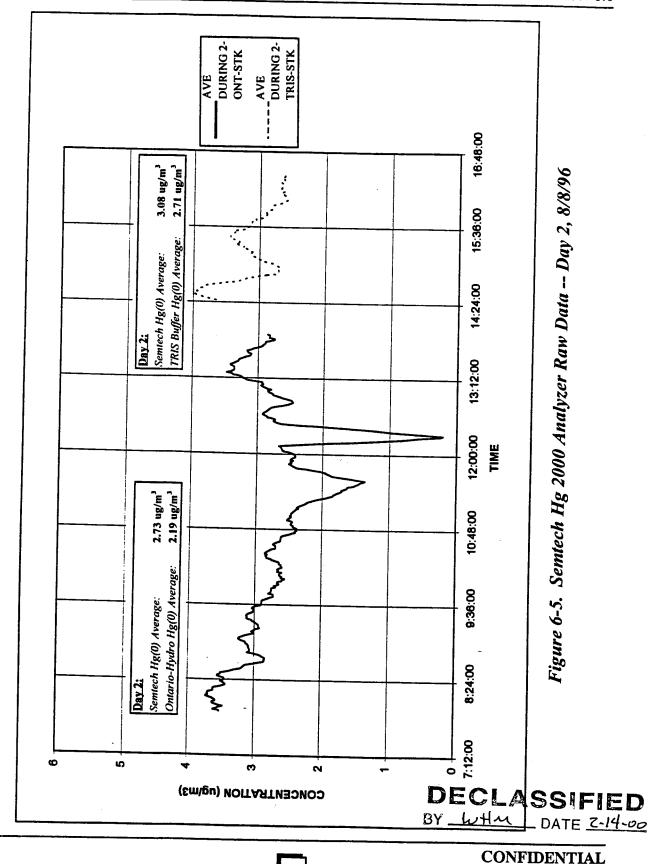


Figure 6-4. Semtech Hg 2000 Analyzer Raw Data -- Day 1, 8/7/96

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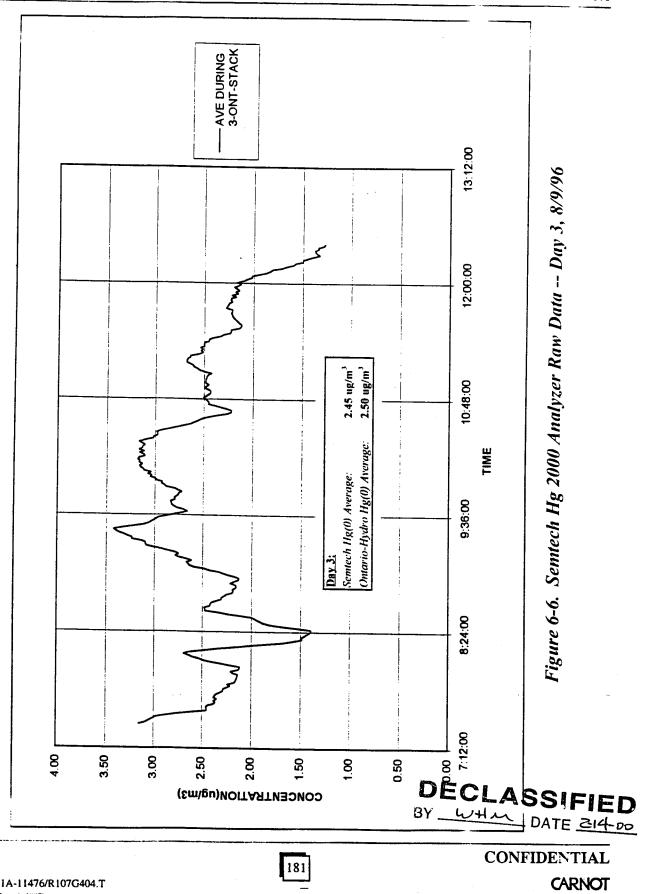


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TABLE 6-13 QUALITY ASSURANCE/QUALITY CONTROL RESULTS EPA METHOD 29 AND FRONTIER GEOSCIENCE METHODS

_		Matrix Sp	ike Analysis		Duplicate Analysi:	5
Test Number	Train Fraction	Matrix Spike Recovery. %	Matrix Spike Duplicate	First Run	Second Run	Relative Difference
			Recovery, %		action	_ %
I-MTLS-OUT	Front-Half	110	110	ND(0.090)	NID(0.000)	
	Back-Half	90	- 89	.ND(0.090) 29	ND(0.090) 30	NC
	MKO	85	85	4.8	30 4.7	3.4
	KMnO ₄ /HCI	100	100	6.3	6.1	2.1
I-MTLS-STK	Front-Half	120	120	ND(0.030)	ND(0.020)	NG
	Back-Half	100	110	2.9	ND(0.030)	NC
	мко .	110	100	0.056	2.9	0.0
	KMnO ₄ /HCI	100	100	0.036	0.046	19.6
		.00	100	13	14	6.9
MESA	Hg(0)	108	101			124
	Hg(11)	97	107			4.6
						4.0
	RAV	V FIELD BLAN	K LABORATORY	DATA		
Test Method			2FB-MTLS-OUT		2FB-MTLS-STK	
-	Fraction		ug/	train		
						
Method 29	Front-Half	ND<0.030	ND<0.030	ND<0.030	0.032	
	Back-Half	ND<0.19	ND<0.19	ND<0.20	ND<0.20	
	MKO	ND<0.010	ND<0.010	ND<0.010	ND<0.010	
	KMnO ₄ /HCl	ND<0.063	0.10	0.22	0.092	
	TRIP BLANK L					
Test Method			Trip Blank 2			
1564	Fraction	. ng/tr				
/IESA	Hg(0)	0.362	0.56			
	Hg(II)	1.23	3.26			
	Quartz Wool/ Probe	2.39	0.134	ng/probe		

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TABLE 6-14
QUALITY ASSURANCE/QUALITY CONTROL RESULTS
ONTARIO-HYDRO AND TRIS BUFFER METHODS

Test Number	Fraction	Spike Result	Spike Level	Spike
		นยู	/L	Recovery, %
DAY 1 8/7/96				
TRIS-FB-SPK-1	TRIS	9.7	10	97
	KMnO4	9.8	10	98
OH-FB-SPK-1	KCI	9.8	10	98
	H2O2	9.6	10	96
	KMnO4	9.5	10	95
DAY 2 8/8/96				
TRIS-FB-SPK-2	TRIS	9.5	10	95
	KMnO4	10.0	10	100
OH-FB-SPK-2	KCl	9.9	10	99
	H2O2	8.4	10	84
	KMnO4	9.8	10	98
DAY 3 8/9/96				
TRIS-FB-SPK-3	TRIS	10.5	10	105
	KMnO4	9.1	10	91
OH-FB-SPK-3	KCl	9.9	10	99
-	H2O2	9.2	10	92
	KMnO4	9.3	10	93



TABLE 6-15 SUMMARY OF FIELD BLANK AND SAMPLE RESULT LABORATORY DATA TRIS BUFFER AND ONTARIO-HYDRO METHODS

			ESP Outlet/	FGD Outlet/			
Test Number		Field Blank	FGD Inlet	Corrected	Stack	Corrected Result,	
	Train Fraction	Level.	Sample Result.	Result,	Sample Result		
		ug/train	ug/train	ug/train	ug/train	ug/train	
DAY 1 8/7/	96						
I-ONT	— KCl Hg(II)	ND(0.05)	36.15	36.15	1.75		
	H2O2 Hg(0)	0.15	1.40	1.25	1.75	1.75	
•	KMnO4 Hg(0)	0.15	12.70	12.55	0.15	0.00	
	Probe Rinse Hg(II) ⁽²⁾	•••	12.70	12.55	13.40	13.25	
	· · · · · · · · · · · · · · · · · · ·						
I-TRIS	TRIS Hg(II)	0.15	4.27	4.12	0.50	0.35	
	KMnO4 Hg(0)	0.05	2.10	2.05	0.50 4.80	0.35	
	Probe Rinse Hg(II)(1)	ND(0.03)	0.28	0.28	· ·	4.75	
	113(11)	(12(0.05)	00	0.28	ND(0.03)	ND(0.03)	
DAY 2 8/8/	<u>96</u>				u.		
2-ONT	KCI Hg(IÍ)	ND(0.05)	28.50	28.50	0.90	0.00	
	H2O2 Hg(0)	ND(0.1)	1.70	1.70	0.90 ND(0.1)	0.90	
	KMnO4 Hg(0)	ND(0.05)	11.62	11.62	13.88	ND(0.1)	
	Probe Rinse Hg(II)	ND(0.03)	4.58	4.58	0.08	13.88 0.08	
				1.20	0.08	0.08	
?-TRIS	TRIS Hg(II)	ND(0.15)	2.60	2.60	0.40	0.40	
	KMnO4 Hg(0)	ND(0.05)	2.80	2.80	5.65	5.65	
	Probe Rinse Hg(II)	ND(0.03)	2.30	2.30	0.05	0.05	
DAY 3 8/9/9	6						
-ONT	<u>v</u> KCl Hg(II)	ND(0.05)	17.40				
= · =	H2O2 Hg(0)	ND(0.03)	17.40	17.40	0.80	0.80	
	KMnO4 Hg(0)	ND(0.1) ND(0.05)	1.85 12.55	1.85	0.30	0.30	
	Probe Rinse Hg(II)	ND(0.03)	9.63	12.55	15.65	15.65	
	115(11)	(U.U3)	7.03	9.63	0.13	0.13	
-TRIS	TRIS Hg(II)	0.30	2.85	2.55	0.30	0.00	
	KMnO4 Hg(0)	ND(0.05)	3.35	3.35	0.30 5.30	0.00	
	Probe Rinse Hg(II)	ND(0.03)	1.63	1.63		5.30	
	J,	_ , ,	1.05	1.05	ND(0.03)	ND(0.03)	

Notes:

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⁽¹⁾ TRIS Probe rinse field blank for Day 1 was not performed, results from Day 2.

⁽²⁾ Probe rinses for the Ontario-Hydro samples were combined with the KCl impinger solution for Day 1 only.

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TABLE 6-15A DISTRIBUTION OF MERCURY WITHIN SAMPLE TRAIN ONTARIO-HYDRO AND TRIS BUFFER METHODS NYSEG POST-RETROFIT TEST PROGRAM -- UNIT 2 AUGUST 1996

Test Method/	Sample Train Fraction							
Sample Location	Mercury Distribution, %							
Ontario-Hydro FGD Inlet FGD Outlet	<u>KCI</u> 52 7	<u>H₂O₂</u> 4 I	KMnO ₁ 27 92	Probe Rinse 17 0				
TRIS Buffer FGD Inlet FGD Outlet	4	TRIS/EDTA 44 5		Probe Rinse 19 0				

Note: Inconsequential amount of mercury found on sample filters.



SECTION 7.0

COMPARISON OF MILLIKEN UNIT 2 POST-RETROFIT CHEMICAL EMISSIONS WITH MAY 1994 BASELINE RESULTS

This section presents a comparison of process stream chemical assessments made during the pre-retrofit or "baseline" test program performed in May 1994 with those from the post-retrofit testing described in prior sections of this report. Comparisons of coal, bottom ash, flyash, and boiler, ESP and stack flue gas test results for Unit 2 are discussed. This section begins with an overview of the retrofits made to the Milliken Station, followed by results comparisons.

7.1 MILLIKEN STATION RETROFIT OVERVIEW

As part of DOE'S Clean Coal Technology Demonstration Program, NYSEG retrofitted Unit 2 after the May 1994 baseline test program with a high-efficiency FGD system for SO₂ emissions control, low-NO_x burners for NO_x emissions control, and ESP and coal mill upgrades for particulate emissions control. The primary objective of this CCTD project is to demonstrate that innovative emissions control technology can be utilized in an energy-efficient manner without a significant impact on overall plant efficiency. The FGD was designed and constructed to control SO₂ emissions by 90-98%. Up to 40% NO_x reduction was targeted for the low-NO_x burners, and the ESP and coal mill upgrades were intended to provide further significant reduction in ESP outlet particulate levels.

7.2 COMPARISONS BETWEEN PRE- AND POST-RETROFIT TEST PROGRAMS

The following tables provide comparisons between the baseline and post-retrofit test programs for various parameters:

Table 7-1: Comparison of Unit Operation and Criteria Pollutant Emissions
Comparison of Coal, Bottom Ash, and Flyash Composition
Comparison of Inorganic Element Flue Gas Emission Levels

Table 7-4: Comparison of Organic Species Flue Gas Emission Levels

Since the FGD was not in operation during the baseline test program, "ESP outlet" baseline emissions are synonymous with "stack" atmospheric emissions. For post-retrofit testing,

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"ESP outlet" concentrations refer to those found after the ESP but prior to the FGD, whereas "stack" emissions are those exiting the FGD to the atmosphere.

Relative percent differences (RPD) are provided on Table 7-2 for each process stream, and on Tables 7-3 and 7-4 for the ESP inlet location. For coal, flyash, and the ESP inlet, RPD values above 25% are considered noteworthy. Differences in bottom ash concentration levels greater than 100% (due to lower concentration levels) should also be noted. Comparisons between ESP outlet and stack flue gas concentrations from the baseline and post-retrofit test programs presented on Tables 7-3 and 7-4 are made using a percent reduction value. The upgrades to the ESP and coal mills, in addition to the installation of the FGD, significantly reduced flue gas concentration levels of target parameters necessitating the use of the percent reduction comparison.

On Tables 7-2 and 7-3, major element emission factors are presented in units of lb/10⁶Btu for coal, bottom ash, flyash, and the ESP inlet, and lb/10¹²Btu for the ESP outlet and stack locations. Highlights from each table are listed below.

Unit Operation and Criteria Pollutant Emissions

- The most notable difference between the baseline and post-retrofit test programs is that baseline testing was conducted while firing a 100% pre-cleaned coal, while a 50/50 mix between raw and pre-cleaned coal was burned during the post-retrofit program.
- The second most notable difference is that the upgrades to the ESP and coal mills improved particulate removal efficiency from 98.95% to 99.88%, reducing ESP outlet particulate concentrations by a factor of 10.
- A 45.4% NO_x reduction can be seen between the two test programs with baseline stack emissions falling from 452 ppm @ 3% O₂ to 247 ppm @ 3% O₂.
- Notable differences in fuel composition and unit operation between the test programs include an increase in fuel sulfur from 1.9% (baseline) to 2.3% (postretrofit), an increase in fuel ash from 7.1% to 9.6%, and a higher boiler O₂ during baseline testing of 3.8% verses 3.1% for the post-retrofit program.

Coal, Bottom Ash, and Flyash Composition

Notable differences between coal and flyash target morganic circum, cadmium, copper, levels for the two test programs can be seen for barium, cadmium, copper,

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manganese, molybdenum, fluorine and most major elements. Additionally for the flyash, antimony, beryllium and selenium differences were above 25%.

• It is not surprising to see such markedly different trace and major element concentration levels between test program coals since concentrations of these elements will vary significantly between raw and clean coal, and also from seam to seam.

Inorganic Flue Gas Emission Levels

- For the ESP inlet, notable differences between concentration levels of target elements are consistent with those seen for the coal and flyash except for chromium (which appears to be due to a high bias in the baseline ESP inlet result). It should be noted that ESP inlet and ESP outlet flue gas selenium levels for both test programs are severely biased low as a result of severe matrix i terferences from sulfur. It should also be noted that the pre-retrofir ESP outlet mercury level is biased high.
- Baseline ESP outlet particulate concentrations were reduced by 88% following the ESP and coal mill upgrades. This reduction in ESP outlet particulate levels directly corresponds to substantially reduced concentrations of trace and major elements exiting the ESP. Baseline ESP outlet trace element concentrations were reduced by 89% (excluding vapor phase elements of mercury, selenium, and anion precursors, in addition to molybdenum), and major element concentrations were reduced by 81%, for an overall reduction in trace and major elements of 86%.
- The large discrepancy between baseline and post-retrofit hexavalent chromium concentrations measured at the ESP inlet suggests that either one or both of the test programs' reported results are in error. Comparisons between mercury species flue gas results were not presented on Table ES-5 due to concerns regarding baseline mercury speciation data validity.
- The apparent increase in ESP outlet molybdenum concentrations for the postretrofit program is not representative of any actual changes in flue gas concentration; rather it is an artifact of blank corrections since molybdenum was found at blank levels for both programs.
- The FGD in combination with the upgraded ESP reduced trace and major element emissions slightly further with an overall reduction in baseline levels of 87% for the same group of elements (with the addition of magnesium). The FGD/ESP

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substantially reduced baseline mercury levels by 71% and baseline chloride, fluoride and sulfur levels by an average of 96%.

• Post-retrofit FGD outlet/stack emissions of magnesium were 53% higher than baseline emissions. This is most likely due to magnesium found within fugitive limestone particles exiting the FGD.

Organic Species Flue Gas Emission Levels

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- With a majority of measured concentrations reported below the analytical detection limit, in addition to detected results existing near or below field blank levels, any comparisons between semi-Vost concentrations from the two test programs is limited.
- The large differences seen for naphthalene between test programs is most likely an artifact of XAD resin degradation rather than any actual change in flue gas levels.
- For the volatile organic elements, the post-retrofit FGD and ESP upgrades combined to reduce baseline benzene emissions by 52%. Post-retrofit FGD outlet/stack emissions of toluene and formaldehyde, however, were 2-3 times higher than baseline emissions.



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TABLE 7-1 COMPARISON OF UNIT OPERATION AND CRITERIA POLLUTANT EMISSIONS PRE- AND POST-RETROFIT TEST PROGRAMS NYSEG MILLIKEN UNIT 2

Unit Type Fuel Type	CE. tangentially-fired Western Pennsylvania Bituminous Coal					
Test Period	Pre-Retrofit	Post-Retrofit				
Test Dates	Measurement Period May 9-13, 1994	Measurement Period August 7-13, 1996				
Fuel Parameters (as-rec'd basis)	,					
Fuel Conditioning	100% Pre-Cleaned	50/50 Blend of Pre-Cleaned/Raw				
Heating Value. Btu/lb	13.012	12,856				
Sulfur Level	1.9%	2.3%				
Ash Content	7.1%	2.3% 9.6%				
Total Moisture Level	7.0%	6.1%				
Coal Flow Rate. klb/hr	114.3	124.4				
Unit Operational Parameters						
Unit Load, MWnet	145.6	148.5				
Boiler O. %	3.8%	3.1%				
ESP Outlet(1) Opacity. %	12	5.9				
ESP Outlet ⁽¹⁾ CO, ppm raw	9.2	5.9 Data Pending				
Air Pollution Control Devices in Or	appation.					
NO _x	None None	Laure NO. Danser				
Particulate	FSP	Low-NO _x Burners				
SO ₂ . Acid Gases	None	Upgraded ESP FGD				
Criteria Pollutant Emissions						
NO_x , dry ppm $\langle \hat{u} \rangle$ 3% O_2 (Stack)	452	242				
NO _x , lb/10 ⁶ Btu (Stack)	· -	247				
Low NO _x Burner Reduction	0.620	0.331 5.4%				
	7-	7.470				
SO ₂ , dry ppm @ 3% O ₂						
Uncontrolled	1454	1741				
Controlled	••	117.5				
FGD Removal Efficiency		93.3%				
Particulate Matter, lb/10°Btu						
ESP Inlet	5.75	6.35				
ESP Outlet(1)	0.060	0.007				
ESP Removal Efficiency	98.95%	99.88%				
FGD Outlet		0.014				
		DECLASS				

Note: (1) For the pre-retrofit test program, ESP Outlet is synonymous with Stack.

BY DATE 2-14-00

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TABLE 7-2 COMPARISON OF COAL, BOTTOM ASH, AND FLYASH COMPOSITION PRE- AND POST-RETROFIT TEST PROGRAMS **NYSEG MILLIKEN UNIT 2**

Target		Coal Feed			Bottom Ash		Flyash		
Parameter	Pre-	Post-	Relative Percent	Pre- Retrofit	Post- Retrofit	Relative Percent Diff.	Pre-	Post-	Relative Percent Diff.
	Retrofit	Retrofit					Retrofit	Retrofit	
	Emissio	n Factors	Diff.	Emissio	n Factors		Emission	n Factors	
T	012-0								
Trace Elements, lb/1		22	1.40/		ND <0.07		31	20	45%
Antimony	26	23	14%	1.4	ND<0.86	 (30)			
Arsenic	426	515	19%	15	7.8	62%	629	509	21%
Barium	2.922	5.579	62%	346	569	49%	2.773	5.005	57%
Beryllium	67	6()	11%	6.4	5.0	26% o	60	46	27%
Cadmium	5.9	3.2	59%	0.31	0.066	129%	7.9	2.5	104%
Chromium	907	809	11%	102	90	13%	816	734	10%
Cobalt	208	191	8%	25	25	()%o	171	176	3%
Copper	381	532	33%	44	53	19%	327	436	29%
Lead	277	287	4%	13	10	24%	271	256	6%
Manganese	1.069	1.439	30%	177	201	13%	885	1.206	31%
Mercury	8.1	7.4	9%	0.01	0.011	48%	0.71	0.57	22%
Molybdenum	76	110	37%	2.8	5.8	70%	79	102	25%
Nickel	621	594	4%	76	88	14%	513	470	9%
Selenium	110	88	22%	ND<0.32	ND<0.52		47	19	87%
Vanadium	1.525	1.201	24%	147	120	20%	1.309	1.099	17%
Anion Precursors, II	5/10 ¹² Btu								
Chlorine	71.153	64.238	10%	ND<14	111		ND<89	636	
Fluorine	4,443	7.005	45%	6.2	22	113%	536	169	104%
Sulfur	1.42E+06	1.79E=06	23%	114	928	156%	25.612	28.336	10%
Major Elements, lb/	<u>10⁶Btu</u>								
Aluminum	0.621	0.759	20%	0.074	0.084	13%	0.517	0.692	29%
Calcium	0.101	0.275	93%	0.012	0.040	104%	0.083	0.251	101%
Iron	0.690	0.918	28%	0.131	0.16	22%	0.499	0.827	49%
Magnesium -	0.024	0.037	40%	0.003	0.0050	57%	0.020	0.036	56%
Phosphorus	0.011	0.017	48%	0.001	0.0019	70%	0.010	0.017	50%
Potassium	0.072	0.094	27%	0.008	0.009	19%	0.060	0.091	41%
Silicon	1.09	1.42	26%	0.134	0.17	22%	0.883	1.350	42%
Sodium	0.021	0.039	60%	0.002	0.0040	62%	0.018	0.034	60%
Titanium	0.021	0.037	21%	0.004	0.0040	10%	0.026	0.034	27%



TABLE 7-3 COMPARISON OF INORGANIC ELEMENT FLUE GAS EMISSION LEVELS PRE- AND POST-RETROFIT TEST PROGRAMS **NYSEG MILLIKEN UNIT 2**

Target		ESP INLET	(1)		ESP OUTLE	FGD OUT	FGD OUTLET/STACK		
Parameter	Pre- Post-		Relative	Pre- Post-			Post-	E1/STACK	
	Retrofit	Retrofit	Percent	Retrofit	Retrofit	Percent	Retrofit	ο.	
	Emissi	on Factors	Diff.	Emissi	on Factors	Reduction ⁽⁴⁾	Emsn. Fetr.	Percent	
Particulate Matter, lb/10	ı <u>é</u> D+ı,		· · · · · · · · · · · · · · · · · · ·					Reduction	
The state of the s	5.75	6.35	10%	0.060	0.007	88%	0.014	77%	
Trace Elements, 1b/10 ¹² B	tu								
Antimony	30	23	26%	ND<0.51	0.19				
Arsenic	475	489	3%	10	1.73	930/	ND<0.08		
Barium	3,051	4,869	46%	8.4	2.1	83%	0.91	91%	
Beryllium	72.3	52	32%	0.76	0.03	75%	1.2	85%	
Cadmium	7.8	3.5	76%	0.76		96%	0.02	97%	
Chromium	894	689	26%	6.2	ND<0.04	87%	0.05	84%	
Hexavalent Chromium		0.85	164%		0.20	97%	0.15	98%	
Cobalt	198	183	8%	ND<0.07	NP		0.63		
Copper	357	475	28%	2.2	0.12	95%	0.12	94%	
Lead	276	309	11%	4.2	0.90	79%	0.69	84%	
Manganese	928	1,373	39%	5.4	0.56	90%	0.63	88%	
Mercury	6.4	6.89	39% 7%	8.1	0.61	92%	1.9	76%	
Molybdenum	78	97	-	8.1	5.74	29%	2.31	71%	
Nickel	592	528	22%	0.17	0.39	-129%	0.35	-108%	
Selenium	58		11%	5.3	0.15	97%	0.33	94%	
Vanadium		26	76%	30	35	-17%	21	30%	
v anadium	1,447	1,129	25%	12	1.1	91%	0.69	94%	
nion Precursors, lb/1012	Btu								
Chlorine	64,476	65,190	1%	69,222	65,159	6%	200		
Fluorine	4,536	6,561	37%	4,259	6,492		398	99%	
Sulfur		1.87E+06	35%	•	1.73E+06	-52%	85	98%	
			3370	1.306+00	1./3E+06	-27%	1.19E+05	91%	
ajor Elements	<u>lb/10</u>	<u>⁶Btu</u>		lb/10	12 Btu		<u>lb/10¹²Btu</u>		
Aluminum	0.624	0.675	8%	4,459	155	97%	61	99%	
Calcium	0.097	0.228	80%	467	196	58%	259	45%	
Iron	0.617	0.821	28%	2,634	85	97%	239	-	
Magnesium	0.024	0.037	45%	68	15	78%	104	99%	
Phosphorus	0.011	0.017	46%	155	66	58%	104	-55%	
Potassium	0.069	0.092 .	29%	452	28	94%	= =	90%	
Sodium	0.021	0.038	60%	364	108	70%	ND<38	91%	
Titanium	0.034	0.035	3%	208	11	70% 94%	141	61%	
•				200	11	94%	6.3	97%	

⁽¹⁾ ESP INLET = flue gas concentrations at the boiler exit or inlet to the ESP.

⁽²⁾ ESP OUTLET = flue gas concentrations at the outlet of the ESP; for the pre-retrofit test program the ESP Outlet and Stack are syn sample locations.

⁽³⁾ FGD OUTLET/STACK = FGD outlet flue gas emissions; only applicable to the post-retrofit test program.

⁽⁴⁾ Percent Reduction of flue gas emissions due to the ESP upgrades = (Pre-Retrofit ESP Outlet Level - Post-Retrofit ESP Outlet

Level)/Pre-Retrofit ESP Outlet Level (5) Percent Reduction of flue gas emissions due to the combined effect of the ESP upgrades and ESP Confer I evel

TABLE 7-4 COMPARISON OF ORGANIC SPECIES FLUE GAS EMISSION LEVELS PRE- AND POST-RETROFIT TEST PROGRAMS NYSEG MILLIKEN UNIT 2

Target	[ESP INLET 11		ESP OUTLET(2)			FGD OUTLET/STACK	
Species	Pre-	Post- Retrofit	Relative Percent Diff	Pre-	Post-		Post-	Percent
	Retrofit			Retrofit	Retrofit	Percent	Retrofit	
	lb/1	0 ¹² Btu		Ib/10) ¹² Btu	Reduction ⁽⁴⁾	lb/10 ¹² Btu	Reduction ¹³
Data that the same								
Polycyclic Aromatic Hydr					**			
Naphthalene	0.69	7 2	165%	0.94	0.1	-908%	10	-1006%
2-Methylnaphthalene	0.052	0.028	58%	0.051	0.027	48%	0.23	-356%
Acenaphthylene	ND<0.003	ND≈0 002		ND<0.004	0.003		ND<0.006	
Acenaphthene	ND<0 005	0.015		ND<0.005	ND<0.057		ND<0 009	
Fluorene	ND<0.015	ND=0.026	•	ND<0.030	ND<0.046		ND<0.035	
Phenanthrene	0.023	0.003	149%	0.134	ND<0.022	84%	0.10	27%
Anthracene	ND<0.006	0.020		ND<0.009	0.014		ND<0.003	
Fluoranthene	ND<0.007	ND<0.002		0.050	ND<0.002	96%	0.008	84%
Pyrene	0.008	ND=0.002		0.009	ND<0.002	78%	ND<0.002	78%
Benz(a)anthracene	ND<0.011	ND=0.002		ND<0.011	ND<0.002		ND<0.002	
through	to	to		to	to		to	
Benzo(g,h,i)perylene	ND<0.033	ND=0.007		ND<0.034	ND<0.006		ND<0.006	
PCDD/PCDF Isomers:								
2378-TCDD	2 5E-06	ND:1.5E-06		2 6E-06	1 8E-06	33%	1.7E-06	34%
12378 PeCDD	ND<1.7E-06			ND 1.6E-06	1.2E-06	J570	ND<1.3E-06	
1234"8 HxCDD	2.4E-06	3.7E-06	43%	2.6E-06	3.4E-06	-29%	3.2E-06	-21%
123678 HxCDD		ND-4 9E-07			ND<4.9E-07		ND<6.0E-07	
123789 HxCDD		ND<6.7E-07			ND<6 9E-07		ND<8.4E-07	
1234678 HpCDD	2.6E-06	2 1E-06	20%	4.8E-06	8.6E-07	82%	ND<8.4E-07 ND<2.1E-06	
OCDD	9.0E-06	9.0E-06	0%	8.5E-06	3.4E-06	60%	6.5E-06	25%
2378 TCDF	ND<1.6F-06	ND-1.9E-06		MDet 0E 06	ND<7.5E-07	••	2.2E-06	
12378 PeCDF	ND<1.7E-06	8.5E-07			ND<7.3E-07			
23478 PeCDF		ND<1.0E-06			ND<8.6E-07		ND<5.8E-07	
123478 HxCDF		ND<9.6E-07		1.8E-06	ND<3.0E-07	 -82%	1.0E-06	
123678 HxCDF		ND-:5.6E-07		= :	ND<9.4E-07		ND<6.6E-07	63%
234678 HxCDF		ND<9.4E-07		-	· - · · · -		ND<3.9E-07	
123789 HxCDF	ND<1.8E-06	2 9E-06			ND<8.0E-07		ND<6.4E-07	
1234678 HpCDF		ND<2.0E-06			ND<4.7E-06		3.1E-06	
1234789 HpCDF		ND<1.3E-06		5.6E-06	ND<7.8E-07	86%	ND<1.1E-06	81%
OCDF	ND<1.9E-00 ND<2.0E-06	1.9E-06	••		ND<8.4E-07		ND<1.4E-06	
OC Dr	ND<2.0E-00	1.91:-00		2.2E-06	ND<1.1E-06	51%	2.4E-06	-11%
olatile Organic Compoun								
Benzene	NP	NP		7.1	6.7	5%	3.4	52%
Toluene	NP	NP		69	56	-717%	19	-177%
formaldehyde	NP	NP		3.6	0.83	77%	8.8	-145%

NP -- measurement not performed.

Notes

CONFIDENTIAL

⁽¹⁾ ESP INLET = boiler flue gas emissions.

⁽²⁾ ESP OUTLET = flue gas emissions exiting the ESP, for the pre-retrofit test program the ESP Outlet and Stack are synonymous sample locations

⁽³⁾ FGD OUTLET/STACK = FGD outlet flue gas emissions; only applicable to the post-retrofit test program.

⁽⁴⁾ Percent Reduction of flue gas emissions due to the ESP upgrades = (Pre-Retrofit ESP Outlet Level - Post-Retrofit ESP Outlet Level)/Pre-Retrofit ESP Outlet Level

Level/Pre-Retrofit ESP Outlet Level

(5) Percent Reduction of flue gas emissions due to the combined effect of the ESP upgrades and FGD = (Pre Ruber & Cutle ASSIFIED Level - Post-Retrofit Stack Level/Pre-Retrofit ESP Outlet Level

BY WHM DATE Z-14-05

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